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of the
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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

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All applications for regular or for associate membership in the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

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ELLWOOD B. SPEAR

Following a heart attack on May 1, 1943, death came suddenly to Ellwood Barker Spear on his farm in Milford, N. H., where he had been living in retirement since 1929. While he was perhaps better known to his colleagues of some years ago than to the younger generation, Dr. Spear was a noted authority on subjects relating to the rubber industry.

Born on February 22, 1875, in Aurora, Ontario, Dr. Spear received his education at the Universities of Manitoba, McGill, Toronto, Leipsig, and Heidelberg; his Ph.D. from the last named institution in 1907. From then until 1920 he was on the staff of the Massachusetts Institute of Technology, as research assistant, instructor, assistant professor, and associate professor of chemistry. In 1920 he became manager of the research department of the Goodyear Tire & Rubber Co. in Akron, Ohio, where he remained until 1922, when he resigned to become chief chemist and vice-president of the Thermatomic Carbon Co., Pittsburgh, Pa. Among his successes in the latter position was the development of "P-33" and other thermatomic carbons. In 1929 he resigned and nominally retired to his farm, but for a year or so was engaged in research and development for the Vultex Chemical Co., Cambridge, Mass.

In World War I, Dr. Spear was a "dollar a year man" in Chemical Warfare, specializing in carbon for gas masks. He was a frequent contributor to chemical literature, and translated Szigmondy's well known work on "Colloid Chemistry", one of the earliest works in that field. Numerous patents on developments of interest to the rubber industry were also issued to him. He was a member of the Chemists' Club of New York, the American Association for the Advancement of Science, and the American Chemical Society. Among his hobbies were dairy farming and the raising of pedigreed dogs.

He is survived by a widow and two nephews.

PAUL I. MURRILL

NEW BOOKS AND OTHER PUBLICATIONS

TREES AND TEST TUBES: THE STORY OF RUBBER. By Charles Morrow Wilson. Published by Henry Holt & Co., 257 Fourth Ave., New York City. 5½ x 8¼ in. 352 pp. $3.50.—Based on personal knowledge and careful research, this book surveys the rubber situation in a realistic practical manner. It acquaints the reader with the Amazon jungles and the islands of the Far East, and with the economic, political and physical aspects of rubber cultivation. It describes work of the pioneers of the modern rubber industry, especially the fundamental work of Charles Goodyear. It describes the extent to which our civilization has become dependent on rubber. And it traces the development of synthetic rubber. While fully acknowledging the superiority of some properties of the newer synthetic rubbers over those of natural rubber, the author takes the position that, despite all the acclaim given to the synthetics, our present crisis would be infinitely less acute if a dependable, permanent supply of natural rubber could be assured. By taking the reader back to the Amazon jungles, where natural rubber began as a world commodity, and recounting the story of what happened in that area, he clearly indicates just how improbable such a solution is and why it will be a long, long time before Amazonian rubber can come to our rescue. The author is a prolific writer, his last book being "Ambassadors in White." Like the latter book, the current one is based on years of first-hand experience in the American Tropics. Furthermore, Mr. Wilson has lived on one of the experimental rubber plantations of Central America, and has closely observed the efforts being made to revive the rubber industry in Latin America. Planned long before the war, the subject matter is up-to-date, even to the inclusion of the complete text of the Baruch Rubber Report. Mr. Wilson combines his facts with an even flow of words, constantly using analogies to convey the meaning of technical rubber terms to the layman. The book has twelve chapters: Rubber Is Vegetable; Rubber Before Goodyear; Charles Goodyear; Amazon Rubber; Malayan and East Indian Rubber; Henry Fordlandia; Synthetics or Elastomers; Our Rubber-Dependent World; Singapore and Japan; Crisis; War and Rubber; Looking Forward. Several of the chapters are illustrated, many of the illustrations being reproductions of photographs taken by the author in his travels. In addition, there is a chronology of Goodyear's life, an extensive bibliography, and a cross-referenced index. [From *The Rubber Age* of New York.]

THE FIVE COMMERCIAL TYPES OF SYNTHETIC RUBBER. Synthetic Rubber Division, U. S. Rubber Co., 1230 Sixth Ave., New York, N. Y. 8½ x 11 in. 40 pp.—As indicated by the title, this booklet is devoted to a discussion of the five commercial types of synthetic rubber—Buna-S, Buna-N, Neoprene, Butyl and Thiokol. Although originally compiled for the sales engineers of the company, it has finally been released for general distribution since it is an accurate statement of the overall synthetic rubber situation, which is not only of value to the rubber industry but presented in such form that it can be understood by the layman. The booklet traces the development of synthetic rubber from laboratory beginnings, describes the properties of commercial synthetics, and relates briefly the part played by U. S. Rubber in their development, manufacture and use in its own products. Of special interest is a chart compiled from the experience of plants and laboratories of the company giving the relative physical and chemical properties of natural rubber and of five types of synthetic rubber. [From *The Rubber Age* of New York.]

REPORT ON THE RUBBER INDUSTRY IN CANADA; 1941. General Manufactures Branch, Census of Industry, Dominion Bureau of Statistics, Department of Trade and Commerce, Ottawa, Canada. 8½ x 11 in. 13 pp. 25c.—As indicated by the title, this publication gives statistics pertaining to the Canadian rubber industry for 1941. It is primarily tables of factual data, such as capital invested, number of employees, salaries and wages, cost of materials used, gross value of production. Specific statistics on tires and tubes and footwear are given. A list of Canadian rubber manufacturers is included. [From *The Rubber Age* of New York.]

TECHNICAL REPORT WRITING. By Fred H. Rhodes, Professor of Chemical Engineering, Cornell University. McGraw-Hill Book Company, Inc., New York, N. Y., 1941. vii + 125 pp. 8 figs. including one of conventional symbols. 15.5 × 23.5 cm. Price, $1.50.—The author, struck, as many others have been, "by the appalling lack of ability of students and graduates to write effective reports," and having concluded that they are unlikely to learn in courses in English how to construct and write a good report, decided that it was up to him to train his students in technical writing by requiring that the reports in his courses be written in good English and subjected "to the same careful criticism that is exercised in the editing of articles for publication in the better technical journals." As there was no satisfactory textbook covering this precise field, he proceeded to write one, and has succeeded admirably in what he set out to do. In a series of brief chapters he outlines the importance of effective presentation, written or oral, of the results of an investigation, particularly where this presentation is to reach the less strictly technical members of an organization, and discusses the characteristics and proper organization of a good technical report, with pertinent remarks on many details of style and usage to which the writer of a report should, but usually does not, pay attention. In these pages I saw no statement with which I do not fully concur, nor any significant omission; and noted only a single error which might puzzle the reader, namely, that on page 99 in the columns headed "deviation" the numbers are the square of the deviation. The last few chapters, occupying more than half of the book, deal briefly with some of the simpler methods of analyzing, correlating, and depicting experimental data; references are given to other books which treat these matters more fully. If ways can be found to induce students—and not only students, but graduates—to absorb, and make use of, the teachings of this book, there should be fewer complaints of poor organization of reports and articles and of sloppy writing which makes it more difficult for the reader to grasp what the writer is trying to convey. [From the Journal of the American Chemical Society.]

A. S. T. M. STANDARDS ON RUBBER PRODUCTS. Prepared by A. S. T. M. Comittee D-11 on Rubber Products. Published by the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa. February, 1943. Paper, 6 by 9 inches, 304 pages. Price $1.75.—This latest edition of "A. S. T. M. Standards on Rubber Products," includes not only new specifications and additions to former regular specifications, but, more significant, eight emergency alternate specifications to conserve rubber. All the emergency alternate specifications apply to insulated wire and cable, and permit use of compounds of lower new rubber content. The May issue of the *A. S. T. M. Bulletin* reports further specifications of this type (ES-28) for chloroprene sheath compound for electrical insulated cords and cables and (ES-30) for the same material when extreme abrasion resistance is not required. These specifications, which are not included in this February, 1943,

volume, were developed since the WPB recently advised the wire industry that the use of rubber for jackets will be prohibited and that Neoprene would be allocated. A total of 41 specifications on general methods, rubber hose and belting; rubber gloves, matting, tape; insulated wire and cable; and latex, rubber cements, sponge and hard rubber products are given. Specification D676—42T on Method of Test for Indentation of Rubber by Means of the Durometer (Tentative) is included for the first time, although the method was accepted by the Society at the annual meeting in June, 1942. Specification D471—43T on Changes in Properties of Rubber and Rubberlike Materials in Liquids, Tests for (Tentative), replaces D471—40T on the same subject. An alternate method for determining increase in volume by linear measurement and specifications for standard control medium which gives aniline point and Saybolt viscosity for the medium are additions found in the new specification. The appendix contains the usual bibliography on sources of information on properties and testing of rubber and a list of the personnel and subcommittees of Committee D-11. [From the *India Rubber World.*]

1942 Book of A.S.T.M. Standards. (In Three Parts). Part I—Metals, 1690 pages. Part II—Non-Metallic Materials—Constructional, 1518 pages. Part III—Non-Metallic Materials—General, 1670 pages. Each part, 6 x 9 in. Published by the American Society for Testing Materials, 260 So. Broad St., Philadelphia, Penna. Prices (cloth binding): Any one part, $9.00; any two parts, $18.00; all three parts, $27.00; Supplements, $3.00 for each part, each year. Note: For half-leather binding add $1.00 for each part and each supplement part.—Issued in three parts as usual, this book of standards contains in their latest approved form all the A.S.T.M. widely used specifications and tests for materials, definitions, and recommended practices. There are 1,090 specifications and standard methods, covering more than 4,900 pages. Continuing the policy first used with the 1939 book (the last one issued, the book being published triennially), this new edition gives all specifications, whether formal standards or tentative. Each part of the 1942 Book has a complete subject index. The Part II index, for example, covers 32 pages, and there are two extensive tables of contents, the first listing all standards under general materials headings and the second listing them in order of sequence of the serial designations. These features are intended to facilitate reference to any subjects covered. Some idea of the large increase in subject matter is indicated by the fact that, whereas the 1939 edition listed 866 standards in 3700 pages, the new edition lists 1090 standards in 4900 pages. Part I of the 1942 Book contains 361 specifications and tests, of which about 200 cover ferrous metals (steel, cast iron, etc.), with the balance applying to nonferrous metals, copper, aluminum, and testing methods. Part II has 425 specifications and tests, many of which are extensively used, including those on cement, brick and building tile and concrete aggregates. Part III has 392 specifications and tests, many of which represent the newer phases of the Society's work, including those on plastics, rubber, soaps and other detergents, and paper and paper products. Specifications for rubber products cover fire hose, belting, gloves, matting, tape, wire and cable, sponge rubber, and hard rubber, while test methods cover analysis, tension, accelerated aging, abrasion, adhesion, set, hardness, and light checking. To keep the books up to date in 1943 and 1944, a supplement will be issued to each part in each of these years. As a special service with the 1942 Book of Standards, there is a complete 200-page Index to Standards which is furnished without additional charge, a copy accompanying the purchase of each part or the complete set. [From *The Rubber Age* of New York.]

A.S.T.M. Standards on Electrical Insulating Materials. Committee D-9 on Electrical Insulating Materials. Published by the American Society for Testing Materials, 260 So. Broad St., Philadelphia, Penna. 6 x 9 in. 441 pp. $2.50.—The large number of standard specifications and testing methods on electrical insulating materials, developed through the work of Committee D-9, comprise this latest edition of standards, with considerable supplementary material. There are groups of specifications and tests on insulating varnishes, paints, lacquers, and their products, and moulded insulating materials, including plastics. The annual report of Committee D-9 and several condensed reports on the significance of tests, as well as an extensive report on "Methods Used for Determination of the Oxidation Tendency of Insulating Oils," are included. Data on rubber blankets, gloves, insulating tape, matting, and hard rubber are brought up to date. There is a carefully compiled, completely cross-referenced index. [From *The Rubber Age* of New York.]

Index to A.S.T.M. Standards. American Society for Testing Materials, 260 So. Broad St., Philadelphia, Penna. 6 x 9 in. 225 pp.—Issued as an adjunct to the 1942 A.S.T.M. Book of Standards, this index enables any of the 1100-odd standard specifications and tests in the volumes to be located readily. It is also of value to those who wish to determine whether the Society has issued standard specifications, testing methods or definitions covering a particular engineering material or subject. All items are listed under appropriate key-words according to the subjects covered. As a convenience, a list of the specifications and tests in numeric sequence of their serial designations is included. [From *The Rubber Age* of New York.]

Organic Reactions. Volume I. Roger Adams, Editor-in-Chief, Werner E. Bachmann, Louis F. Fieser, John R. Johnson and H. R. Snyder. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1942. vii + 391 pp. 15.5 × 23.5 cm. Price, $4.00.—Organic chemists will welcome this first volume of the series with more than ordinary enthusiasm, for it is a landmark in the literature of organic chemistry. The series is a new departure, and will make available extremely valuable information in a readily applicable form. Perhaps the nearest approaches to the present series are the still useful but quite out-of-date special parts of Houben-Weyl and Lassar-Cohn on general organic reactions such as condensation, nitration, etc. Primarily, the work is concerned with the scope and limitations of important laboratory reactions. "The subjects are presented from the preparative viewpoint, and particular attention is given to limitations, interfering influences, effects of structure, and the selection of experimental techniques. Each chapter includes several detailed procedures illustrating the significant modifications of the method." The textual material, tables and extensive bibliographies provide a coverage that is as nearly complete as one might wish. The twelve chapters have been written by authors who have had particular experience with the reactions or processes described: (1) "The Reformatsky Reaction" (Ralph L. Shriner); (2) "The Arndt-Eistert Synthesis" (W. E. Bachmann and W. S. Struve); (3) "Chloromethylation of Aromatic Compounds" (Reynold C. Fuson and C. H. McKeever); (4) "The Amination of Heterocyclic Bases by Alkali Amides" (Marlin T. Leffler); (5) "The Bucherer Reaction" (Nathan L. Drake); (6) "The Elbs Reaction" (Louis F. Fieser); (7) "The Clemmensen Reduction" (Elmore L. Martin); (8) "The Perkin Reaction and Related Reactions" (John R. Johnson); (9) "The Acetoacetic Ester Condensation and Certain Related Reactions" (Charles R. Hauser and Boyd E. Hudson, Jr.); (10) "The Mannich Reaction" (F. F. Blicke); (11) "The Fries Reaction" (A. H. Blatt); and (12)

"The Jacobsen Reaction" (Lee Irvin Smith). Some of the chapters have many more formulas in the tables than others. A strictly uniform pattern of presentation may not be the best procedure for a work of this kind, but a more extensive use of formulas instead of names in some of the chapters would be preferred by students and others. It is interesting to note the occasional cases where "name" reactions bear the name, not of the original discoverer, but of one who subsequently explored the broad aspects of the reaction. The series, separate volumes of which will appear periodically, will form something more than a mere adjunct to laboratory procedures. It is the sort of work that not only stands alone, but that will prove an invaluable supplement to every text or reference work in organic chemistry. With the appearance in recent years of a wide variety of excellent books on organic chemistry, the content of some seminar and special topics courses may be revised to place added emphasis on immediately current articles instead of extensive surveys which are increasingly available. Although this work appears in war times, the general idea was conceived several years ago, and in this respect is unlike "Organic Syntheses", the origin of which is directly traceable to meeting the needs for research chemicals in the last war. The editors and authors are to be complimented and thanked for a splendid work which must have made unusual demands on them in these strenuous times. [From the *Journal of the American Chemical Society.*]

THE GAS MASK. Office of the Chief of Chemical Warfare Service, War Department, Washington, D. C. 6 x 9 in. 24 pp.—Issued as Booklet No. 1 of the series of educational booklets planned by the Chemical Warfare Service to acquaint the public with its specialized work, this booklet is an illustrated digest of the history and development of the military gas mask. The training mask, military service mask, diaphragm mask, optical mask, and other types are described and illustrated, with brief mention of the masks used by the Axis partners. [From *The Rubber Age* of New York.]

HARDNESS. By D. Landau. Nitralloy Corporation, 230 Park Ave., New York, N. Y. 6 x 9 in. 108 pp.—The French engineer, P. Roudie, has shown that, by adopting a dynamic method of hardness testing, he could as a consequence define hardness as a quantity of energy and, therefore, as a function of the three fundamental units of mass, length and time. This booklet amplifies Roudie's method. The subtitle of the booklet, "A Critical Examination of Hardness, Dynamic Hardness, and an Attempt to Reduce Hardness to Dimensional Analysis", makes clear the subject matter. An extensive bibliography on hardness is included. [From *The Rubber Age* of New York.]

THE ELECTRON MICROSCOPE. By E. F. Burton, Head of the Department of Physics, University of Toronto, and W. H. Kohl, Development Engineer, Rogers Radio Tubes Limited, Toronto. Reinhold Publishing Corporation, 330 West 42nd Street, New York, N. Y., 1942. 233 pp. Illustrated. 15.5 × 23.5 cm. Price, $3.85.—Great things are expected of the electron microscope as a tool of the investigator in pure and applied research. Like all things not well understood, it has sometimes been the subject of overenthusiastic expectations. On the other hand, a lack of comprehension of the instrument operates to delay the useful applications to which it may be put. In this volume, the authors by simple steps lead the reader gradually to a comprehension of the nature of vision and the elements of optical science, through a brief course in electronics and its branch called electron optics, the basis of taking magnified pictures without light. This is a book for the thoughtful

reader, not a picture book. Copiously illustrated, however, with homely diagrams, adequate although executed with nonprofessional draftsmanship, and with half-tone reproductions of photo and electron micrographs, it presents a physicist's explanation of the theory and operation of this modern instrument in a manner easily comprehended by scientists in fields other than that of electronics. For the lay reader who enjoys a certain amount of homework, the thoughtful study of this volume will present much that is authentically and interestingly informing in various fields of life of today and of tomorrow. [From the *Journal of the American Chemical Society.*]

ADHESIVES. Felix Braude. Chemical Publishing Co., Inc., 234 King St., Brooklyn, N. Y. 1943. Cloth, 5¼ by 8½ inches. Index. 168 pages. Price $3.—Presented from the practical point of view with a minimum of theoretical discussion, this book was designed primarily for the producer, consumer, or salesman. The theory and the application of adhesives and tests for adhesives are first discussed; then the major raw materials, such as flour, dextrins, casein, gums, resins, etc., are covered as to source and general chemical classification. The chapters on the different types, which include one on rubber dispersions and solutions as adhesives and one on rubber adhesives (solvent cements), contain many examples of formulas for specific applications. Reasonably detailed mixing instructions are supplied in most cases, and a chapter on equipment for the manufacture of adhesives is also included. (From the *India Rubber World.*]

PRACTICAL EMULSIONS. By H. Bennett. Chemical Publishing Co., Inc., 26 Court St., Brooklyn, N. Y. 5½ x 8½ in. 452 pp. $5.00.—A practical book written for the practical worker. It touches only lightly on the theoretical aspects of colloidal chemistry, leaving this complex subject to the several excellent books available, and concentrates on the art of making and applying emulsions. The author has not attempted to compile a complete record of all published works on emulsions, but gives sufficiently diverse examples to illustrate the advances in this field. Because emulsions are used in so many varied fields, from textiles to pharmaceuticals, the book, of necessity, covers a wide range. The book is divided into two sections, the first devoted to general information, the second to formulas. There are 31 chapters, nine in the first section, twenty-two in the second. In addition, there is a completely cross-referenced index. Brief mention is, of course, made in various chapters to rubber and latex dispersions and emulsions, one chapter being devoted to "Resin and Rubber Emulsions". Included among the formulas in the latter chapter are those for rosin, resin, paraffin rosin, Cumar, ethylcellulose, methyl methacrylate, cellulose ester, polystyrene resin, and Vinylite emulsions. In many cases more than one formula is given. [From *The Rubber Age* of New York.]

PLASTICS—FROM FARM AND FOREST. By E. F. Lougee. Plastics Industries Technical Institute, 221 No. La Salle St., Chicago, Ill. 4½ x 6¾ in. 157 pp. $2.00.—As stated in the preface, this interesting little book was not written for those who know plastics, but for those who know little or nothing about the subject but would like to learn more. Stress is placed on the versatility of the present-day plastics, how broad their scope really is, and how far-reaching their applications in service are likely to become. In the latter respect, Mr. Lougee says that this is due largely to the fact that plastics are chemical compositions which can be tailor-made in the laboratory to fit specific needs. The growing alliance between agriculture as a source of raw materials

and industry, which has been manifest for many years, is skillfully traced. Avoiding the technicalities of chemical or mechanical processes, the author outlines some of the important uses of farm and forest products in industry and reviews them to emphasize how farm chemurgy and research have been put to work during the present generation. Rubber comes in for consideration, and an entire chapter is devoted to guayule and various rubberlike materials, including the Bunas, Neoprene, Thiokol, Koroseal and Resistoflex. The book has 10 chapters, and contains a list of experiment stations maintained by the U. S. Department of Agriculture. Mr. Lougee, the author, is a former editor of *Modern Plastics*, and has served as Chairman of the Advisory Board of the Plastics Institute since its formation in 1940. [From *The Rubber Age* of New York.]

NOXIOUS GASES and the Principles of Respiration Influencing Their Action. Second and Revised Edition. Yandell Henderson and Howard W. Haggard. Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. 1943. American Chemical Society Monograph Series. Cloth, 6 by 9 inches, 294 pages. Bibliography and subject index. Price $3.50.—Volatile substances are used in modern industry in enormous quantities as raw materials, as products, and as agents of manufacture, and the gas hazards of modern industry and the defenses against them are extremely important. This book deals primarily with the toxic action which depends on volatility. Only gases which occur in industry are dealt with in this volume; their use in war is not discussed. The book was written for the practical use and information of chemists, engineers, and others engaged in industry; therefore a rather full description of the function of respiration is included. Of special note are the chapters on resuscitation and the prevention of poisoning by noxious gases. Gases are classed as irritants, asphyxiants, and volatile drugs and druglike substances, and are discussed in detail in various chapters according to this classification. For quick reference, a table of 200 noxious gases listed according to chemical composition and classified according to their action is included. This table refers to the chapter in the book where detailed information may be found. In these days of the introduction into the rubber industry, of new chemicals, many of which are volatile in character, and new processes, and because of the use of new personnel in old processes where volatile substances are used, this book should be of considerable value. [From the *India Rubber World*.]

SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY, DETROIT, MICH.,

APRIL 15–16, 1943

The Division of Rubber Chemistry convened in Detroit, April 15–16, as a part of the 105th Meeting of the American Chemical Society. Although originally scheduled for Indianapolis, this meeting was changed to Detroit because of inadequate housing facilities in the former city. The headquarters of the Division were at the Book-Cadillac Hotel.

The interest in the program of the Division, held in the Masonic Temple, exceeded all expectations. The attendance averaged around 600, and reached a record of over 1100 during the presentation of the Charles Goodyear Lecture by L. B. Sebrell.

In opening the papers program, Chairman Blake pointed out that the rubber industry is being revolutionized by the war. Problems growing out of this rapid change have been manifold and difficult. He expressed confidence in our ability to solve them and optimism as to the accomplishments of this period. The following papers were presented:

1. Molecular Weights of High Polymers. Maurice L. Huggins.
2. Heat Generation in Rubber Due to Flexing. S. D. Gehman, P. J. Jones, and D. E. Woodford.
3. Flex-Life and Crystallization of Synthetic Rubber. J. H. Fielding.
4. Properties of Blends of Thiokol Synthetic Rubber Type-FA with Neoprene-GN, Hycar-OR, and Perbunan. S. M. Martin, Jr. and A. E. Laurence.
5. Charles Goodyear Lecture. L. B. Sebrell.
6. Thirty Years of Contributions to the Science of Synthetic Rubber. W. L. Semon.
7. A Laboratory Technique for Experimental Polymerization of Synthetic Rubber. C. F. Fryling.
8. Vulcanization of GR-I (Butyl Rubber). A. A. Somerville.
9. Conductivity of Rubber and Synthetic-Rubber Tread Stocks. Leonard H. Cohan and Martin Steinberg.
10. Heat Resistance of Neoprene Type-GN Vulcanizates. Don B. Forman.
11. Simple Vulcanizates of Buna-S and Sulfur. I. Physical and Chemical Properties. La Verne E. Cheyney and Arthur L. Robinson.
12. Carbon Black in Butyl Rubber. L. B. Turner, J. P. Haworth, Winthrope C. Smith and R. L. Zapp.
13. The Brittle Point and Shatter Point of Some Rubberlike Compositions. Glenn E. King.
14. Report of Crude Rubber Committee. George A. Sackett.
15. Evaluation of Butadiene in the Presence of Other Unsaturated and Saturated Gaseous Hydrocarbons. J. F. Cuneo and R. L. Switzer.
16. Density of Carbon Black by the Helium Displacement Method. R. P. Rossman and Walter R. Smith.
17. Unsaturation of Butadiene and Related Polymers as Determined by Iodine Chloride Addition. A. R. Kemp and H. Peters.
18. Variation of pH Attributable to Phase Distribution in Synthetic-Rubber Emulsion Polymerization Systems. C. F. Fryling and E. W. Harrington.
19. Effect of Petroleum Products on Neoprene Vulcanizates. IV. Effect of Gasolines. Donald F. Fraser.
20. Polar-Compound Treated Fatty Oils for Rubber. Laszlo Auer.

In addition to the above list, two papers originally scheduled were withdrawn by the authors: (1) Agripol, A New Chemurgic Rubber Substitute, by Andrew J. Snyder and Clinton A. Braidwood, and (2) Effect of Time and Temperature of Cure on Properties of GR-S Tread Stocks, by B. S. Garvey, Jr. and A. E. Juve.

The Charles Goodyear Lecturer, L. B. Sebrell, was introduced by A. R. Kemp, who had served as Chairman of the Committee which, in 1939–1940, drew up the rules governing this lecture award. Inasmuch as David Spence, the first recipient of this award, was prevented by illness from giving his lecture in 1941, Sebrell's paper, "The Second Mile", was the first presentation of the lecture before the Division of Rubber Chemistry.

The activities of the Crude Rubber Committee, according to George Sackett, Chairman, have been reduced greatly by the War. This Committee has made

outstanding contributions to the rubber industry in the past in the excellent work it has done in raising the quality of plantation crude rubber. In answer to the question as to how the Committee can best serve under present conditions, it was announced that it plans (1) to evaluate the non-*Hevea* natural rubbers as soon as they become available in quantity, and (2) to undertake a similar study of the various synthetic elastomers as soon as these new raw materials become stabilized in method of production and are available in volume.

At the business meeting, A. R. Kemp, in the absence of the Chairman of the Nominating Committee, presented the following list of nominations for officers for 1943–1944:

Chairman	Harold Gray
Vice-Chairman	Fred Amon
	W. A. Gibbons
	W. W. Vogt
Secretary	Howard Cramer
Treasurer	C. W. Christensen
Sergeant-at-Arms	M. J. DeFrance
	Bruce Silver
Directors:	J. H. Doering
	R. F. Dunbrook
	F. W. Frerichs
	George Haslam
	A. H. Nellen
	J. H. Osterhof
	M. G. Shepard

The report of the Nominating Committee was approved, without additional nominations from the floor. The election will be conducted by letter-ballot and the results announced at the Fall Meeting.

The Buffalo Rubber Group and the Ontario Rubber Section of the Canadian Chemical Association held a joint luncheon, with Burt Wetherbee, Chairman of the Buffalo Group, presiding. Among those present were J. C. Howard, Chairman of the Ontario Rubber Section, A. B. Lewis, Vice-Chairman of the Rubber and Plastics Division of the Montreal Section of the Society of Chemical Industry, P. K. Frolich, Chairman of the American Chemical Society, J. H. Doering, Chairman of the Detroit Rubber Group, and the Chairman and Secretary of the Division of Rubber Chemistry.

The Divisional Banquet was held in the ballroom of the Book-Cadillac Hotel. The 725 members and guests in attendance were privileged to hear a most challenging and inspiring talk by C. F. Kettering, of the General Motors Corporation, on "Research in the Rubber Industry". The Division is indebted to J. H. Doering, Chairman of the Detroit Rubber Group, and his Committee for their fine handling, not only of this function, but also of the general arrangements for the Divisional meeting.

The Chairman announced that the Executive Committee had decided that the Division would meet somewhere in the coming autumn. However, in view of the Society's not having announced its selection of a meeting place for its Fall Convention, the question where the Division should convene was still under consideration

H. I. Cramer
Secretary

RUBBER, POLYISOPRENES AND ALLIED COMPOUNDS

II. THE MOLECULE-LINKING CAPACITY OF FREE RADICALS AND ITS BEARING ON THE MECHANISM OF VULCANIZATION AND PHOTO-GELLING REACTIONS *

ERNEST HAROLD FARMER AND STEPHEN E. MICHAEL

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Ostromislensky[1] discovered that benzoyl peroxide when heated with rubber to 140° brought about a species of vulcanization of the rubber, the chemical nature of which has been the subject of much conjecture and experimental investigation. It was thought at first that the process was essentially one of oxidation and, indeed, free benzoic acid derived from the peroxide was isolated by Ostromislensky from the reaction product; but van Rossem, Dekker, and Prawirodipoero[2] found that, although much benzoic acid was liberated during the reaction, some became united with the rubber, and could afterwards be freed by saponification. Van Rossem and his collaborators, however, were unable to correlate the accumulated observations with the previously published generalizations of Gelissen and Hermans[3] concerning the nature of the reactions between benzoyl peroxide on the one hand and numerous substances, including alcohols, organic acids, and saturated and benzenoid hydrocarbons, on the other; nevertheless, they agreed with Gelissen and Hermans on one point, *viz.*, that to some extent cleavage of the peroxide with formation of benzoic acid probably occurred, and they suggested that the concomitant reaction was a dehydrogenation of the rubber, the latter possibly becoming cross-linked as a result ($2C_5H_8 + PhCO\cdot O\cdot O\cdot COPh \rightarrow —C_5H_7\cdot C_5H_7— + 2PhCO_2H$). Subsequently, Ostromislensky[4], following useful observations by Bock[5], made a new examination of the reaction, and concluded that it proceeded according to the equation:

$$(C_5H_8)_n + n\text{PhCO}\cdot\text{O}\cdot\text{OCOPh} \rightarrow n\text{PhCO}_2\text{H} + (C_5H_7\text{OCOPh})_n$$

If this view is correct, the net result of the interaction must be the substitution of a benzoate group in each reacting isoprene unit of the rubber chain, presumably without decreasing materially the number of the original double bonds. Evidence that the reaction does indeed occur without substantial diminution in the original unsaturation had earlier been contributed by Fisher and Gray[6].

In view of recent developments relating to the formation of free radicals during the thermal decomposition of dry or dissolved benzoyl peroxide[7], it appeared fairly certain that Ostromislensky's equation is an oversimplified representation of the phenomena involved. For further advance in the matter, however, it seemed desirable to examine in some detail the possibilities of reaction between benzoyl peroxide and some convenient simple olefin. That simple

* Reprinted from the *Journal of the Chemical Society*, 1942, pages 513–519.

olefins readily react with benzoyl peroxide was effectively shown by Lippmann[8], who heated amylene with the peroxide at 100°, and obtained definite (although doubtless incorrectly identified) products[9]; that the scope for the exercise of such reactivity is wide is already apparent from the ever-increasing list of condensations and "polymerizations" among olefinic substances which can be promoted by benzoyl peroxide and other peroxidic substances. The simplest analog of rubber is trimethylethylene, $H[CH_2CMe{:}CHCH_2]H$, but since in this hydrocarbon the α-methylene groups are somewhat modified in character by being incorporated in methyl groups, cyclohexene was chosen for examination in its place.

When a large excess of cyclohexene was heated with benzoyl peroxide to 140° in a closed vessel, all the peroxide disappeared, and most of its substance entered into combination with the cyclohexene. Carbon dioxide was formed during the reaction, with resulting increase of pressure. The reaction product contained some benzoic acid, but no significant proportion of any other acidic substance. The neutral portion of the product consisted of a number of hydrocarbons of the C_6 and C_{12} series, and various benzoates derived from these hydrocarbons.

If the free-radical basis of the thermal decomposition of benzoyl peroxide as advanced by Hey and Waters is accepted, the radicals to be expected from the decomposed peroxide are Ph^- and $PhCOO^-$, and these may be expected to react with the very abundant cyclohexene molecules, either (1) extracting hydrogen atoms from them and so forming cyclohexenyl radicals and radical hydrides RH (where R = Ph or PhCOO)·

$$(1)\ C_6H_{10} + R^- \rightarrow C_6H_9^- + RH \quad (2)\ C_6H_{10} + R^- \rightarrow C_6H_9R + H^-,$$

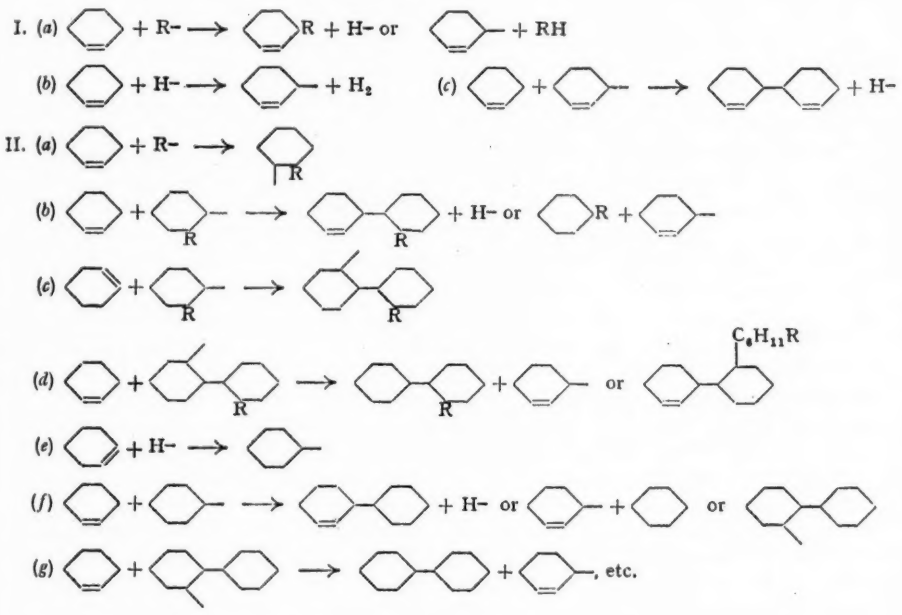
or (2) expelling hydrogen atoms from them and themselves coupling with the resulting residues. Any olefin, however, which contains the group, $—CH_2CH{:}CH—$, has two outstanding characteristics: (1) the exceptional ease with which α-methylenic hydrogen atoms can be detached[10], and (2) the usual high reactivity of the double bond. The first characteristic is likely to ensure that, in spite of the general capacity of a free radical to displace a hydrogen atom from any saturated carbon atom in the cyclohexene ring, the actual displacement will occur at one of the α-methylene groups. The second characteristic is of somewhat uncertain importance in the present connection, since there is no very clear evidence to show how far attack by free radicals at the double bond in the manner (3) is likely to succeed, although recent investigations indicate that bromine atoms by adding at one end of an

$$(3)\ —CH{:}CH— + R^- \rightarrow {}^-CHCHR$$

ethylenic bond can initiate the "abnormal" type of hydrogen bromide addition to olefins[11], the *cis-trans* rearrangement of stilbene[12], and a species of oxygen addition to olefins[13]; also that sulfite radicals in a similar way can initiate the addition of sodium sulfite to olefins[14], and likewise radical-molecules probably unite with olefin molecules and give, by repetition of the process, long macropolymeric chains[15].

If a reaction according to (3) does occur to an appreciable extent, the number of possible products from benzoyl peroxide and cyclohexene will be considerably increased, and the main lines of reaction are then likely to include

the following specific reactivities[16], in which R^- represents a free radical derived by decomposition of dibenzoyl peroxide.



Since R^- = Ph^- or $PhCOO^-$, the products according to (I) should be: benzene, benzoic acid, Δ^2-cyclohexenyl benzoate, 3-phenyl-Δ^1-cyclohexene, and $\Delta^{2'}$-cyclohexenyl-Δ^2-cyclohexene; those according to (II) should be: 2′-phenylcyclohexyl-Δ^2-cyclohexene, 2-$\Delta^{2'}$-cyclohexenylcyclohexyl benzoate, phenylcyclohexane, cyclohexyl benzoate, 1-phenyl-2-cyclohexylcyclohexane, 2-cyclohexylcyclohexyl benzoate, Δ^2-cyclohexenyl-[cyclohexyl-2′]-[cyclohexyl-2″] benzoate, Δ^2-cyclohexenyl-[cyclohexyl-2′]-[cyclohexyl-2″]-benzene, 3-cyclohexylcyclohexene, cyclohexane, cyclohexylcyclohexane, etc.

The reaction products actually isolated or otherwise identified are shown in italics in the above list, but in addition to these, cyclohexane and cyclohexylcyclohexane, which would be difficult to recognize in the mixture, may well have been present in appreciable amount; phenylcyclohexane also may have been present in minor amount. The presence of cyclohexylcyclohexene is doubtful. Tricyclic reaction products were not well represented, but in the highest-boiling fractions obtained from the reaction mixture the principal component (cyclohexenylcyclohexyl benzoate) appeared to be admixed with appreciable proportions of tricyclic hydrocarbons. The substances which were found to be present in largest proportion were benzoic acid, cyclohexenyl benzoate, cyclohexyl benzoate, cyclohexenylcyclohexene, and cyclohexenylcyclohexyl benzoate, but benzene, the yield of which could not be reliably determined, was probably also a major product.

A number of conclusions are to be drawn from the character and quantitative proportions of the chief reaction products. (1) The main bulk of the free radicals formed by decomposition of the peroxide attack the olefin molecules at the α-carbon atoms, although some not inconsiderable degree of attack

apparently succeeds at the double bond. (2) It is clear that about half the PhCOO— groups present in the peroxide (2 per molecule) survive in the form of benzoates, but it is not clear whether all the peroxide molecules decompose in fashion (A) or whether some can decompose in fashion (B). (3) The interlinking of hydrocarbon molecules, whether it occurs by the action of olefin or

$$\text{(A)}\quad \text{PhCO}\cdot\text{O}\cdot\text{OCOPh} \rightarrow \text{PhCO}\cdot\text{O}\cdot + \text{CO}_2 + \text{Ph}—$$
$$\text{(B)}\quad \text{PhCO}\cdot\text{O}\cdot\text{OCOPh} \rightarrow 2\text{PhCO}\cdot\text{O}—$$

hydroölefin free radicals on ordinary olefin molecules (*e.g.*, reactions I*c*, II*f*, II*g*), or of benzoate-substituted or phenyl-substituted hydroölefin radicals on ordinary olefin molecules (*e.g.*, reactions II*b*, II*c*, II*d*), constitutes a very large proportion of the total reactivity observed. (4) Interlinking of olefin molecules is confined almost entirely to the "dimeric" stage of reaction, although a little phenyl-substituted "dimer" appears to have been formed. (5) Cyclohexenylcyclohexenyl benzoate, $C_6H_9\cdot C_6H_8OCOPh$, occurs among the minor reaction products, but does not appear in schemes I or II; hence it is necessary to conclude that cyclohexenylcyclohexene, $C_6H_9\cdot C_6H_9$, which is formed in considerable yield, is subsequently attacked to some small extent by benzoate radicals.

In view of these results, it is not surprising that the action of benzoyl peroxide on rubber consists largely in the attachment of numerous benzoate groups to the carbon chain (to a maximum of one benzoate group per unit), without material destruction of the original unsaturation of the rubber being caused. These groups doubtless become substitutionally attached at one or other of the α-carbon atoms of the isoprene units, but probably mainly at the α-methylene groups adjoining the methylated carbon atoms, thus:

$$—\text{CH(OBz)CMe}:\text{CHCH}_2\text{CH(OBz)CMe}:\text{CHCH}_2—$$

This substitution will, however, be only one of the two main results of the reaction with benzoyl peroxide, the second of which will involve the linking together of the rubber chains—probably largely at the α-methylene groups (usually the α-methylene groups adjoining the methylated carbon atoms) as in (*h*), but probably to some extent also at an ethylenic carbon atom in one of the interlinking units, as in (*j*) or (*k*), and possibly to some minor degree in one of the other ways typified in the reactions II, (*a*)–(*g*). Some small degree of phenyl substitution in the unlinked chains according to reaction I(*a*) is also likely to occur.

$$\begin{array}{l} —\text{CHCMe}:\text{CHCH}_2— \\ \quad\quad\quad\quad\quad (h) \\ —\text{CHCMe}:\text{CHCH}_2— \end{array} \qquad \begin{array}{l} —\text{CHCMe}:\text{CHCH}_2— \\ \quad\quad\quad\quad\quad (j) \\ —\text{CH}_2\text{CMeCH(OBz)CH}_2— \end{array}$$

$$\begin{array}{l} —\text{CHCMe}:\text{CHCH}_2— \\ \quad\quad\quad\quad\quad (k) \\ —\text{CH}_2\text{CHCMe(OBz)CH}_2— \end{array}$$

As regards the widespread use of benzoyl peroxide and other peroxides for promoting chemical aggregation, "polymerization" or "condensation" of many different types of molecules, there is every reason to believe that free radicals from the decomposing peroxide initiate the cross-linking, which can be continued by chain reactions.

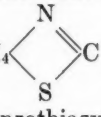
It might be anticipated that other compounds which break down either spontaneously or on heating to give free radicals would have an action on

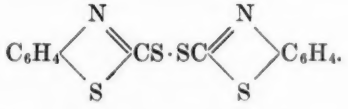
olefins (and particularly on rubber) precisely analogous to that of benzoyl peroxide. It is not surprising therefore to find that diazo compounds, whose strong tendency to break down to give free radicals and gaseous nitrogen is now well recognized[17], are active vulcanizing agents[18] for rubber. Buizov worked with diazoaminobenzene, but later Levi[19] found that all diazoamino compounds of the constitution $RN:NNXR'$, where R is an aryl group, R′ is an aryl, aralkyl or arylamino group, and X is hydrogen, a metal, an alkyl, acyl, aryl or aralkyl group, are vulcanizing agents. Also Levi observed that diazo compounds which were effective vulcanizing agents evolved nitrogen when they are heated to the usual vulcanization temperature (approximately 140°)[20], and oxidation plays no part in the vulcanizing reaction. The reality of the active participation of free radicals is to be deduced from Levi's observation that diazoaminobenzene when heated alone at 150° gave 1 mol. of nitrogen and both *o*- and *p*-aminobiphenyl, a decomposition which may be represented:

$$PhN:NNHPh \rightarrow Ph^- + NHPh^-$$
$$Ph^- + NHPh^- \rightarrow PhC_6H_4NH^- + H^- \rightarrow PhC_6H_4NH_2$$

Furthermore, Fisher[21] has found, not only that 2, 4, 6, 2′, 4′, 6′-hexachlorodiazoaminobenzene readily vulcanizes rubber, but that some of the reagent (which presumably means fragments of the reagent molecules) adds to the rubber, giving some hexachlorodiphenylamine as a byproduct.

The symmetrically substituted diphenyl- and tetraphenylhydrazines are known to decompose readily into free radicals, and these are found to produce a stiffening effect on rubber when kneaded into it. On the contrary, monosubstituted alkyl- and arylhydrazines, as well as *as*-diphenylhydrazines, act as softeners of rubber[22], from which it may be deduced that they are promoters of oxidation, presumably functioning for this purpose in a manner similar to pyridine[23].

Perhaps, however, the most interesting example of an effective vulcanizing agent is tetramethylthiuram disulfide, $CHMe_2CS\cdot S\cdot SCSCHMe_2$, which is a close sulfur analog of benzoyl peroxide. The capacity of this substance to yield free radicals spontaneously or on heating has, as far as we are aware, not been demonstrated, but it is remarkable that this disulfide is not only by itself an excellent vulcanizing agent for rubber, but is a first-rate accelerator of sulfur vulcanization. The method of action of accelerators has never been determined, but it seems not unlikely that the effectiveness of at least some of them is due to their capacity to yield free radicals spontaneously or on heating, either when used in the form of their zinc salts, *e.g.*, dithiocarbamates, $R_2NCS\cdot SH$ and thiolbenzothiazole,  , or when used directly, *e.g.*, tetramethylthiuram disulfide and benzothiazyl disulfide,



Ostromislensky's reaction between benzoyl peroxide and rubber appears to involve two distinct features, *viz.*, the interlinking of rubber units (which process may be inter- or intramolecular and so take the form of cross-linking

of molecules or cyclization reactions), and the addition of fragments to the rubber chain. This dual type of reaction probably extends also to sulfur vulcanizations, and to vulcanizations in which the action of sulfur is assisted by an organic accelerator. The exact course of reaction in either of these cases is uncertain, but in both cases the production of a satisfactory vulcanized structure as determined by a physical test (the tensile strength[24]) is but little dependent on the loss of original unsaturation in the rubber. Thus Brown and Hauser[25] found that the optimum (physical) state of vulcanization of rubber obtained when tetramethylthiuram disulfide is the vulcanizing agent, *i.e.*, when no free sulfur is used, occurs when less than 2 per cent of the original rubber-unsaturation has been lost, and an average of 0.25 atom of sulfur per C_5H_8 unit has been incorporated in the rubber chain. At this point, chemical incorporation of sulfur in the rubber stops, and if heating at the vulcanization temperature (141°) is continued, it causes little further diminution in unsaturation. When the vulcanizing agent is sulfur, used in conjunction with a small proportion of active accelerator, the loss of unsaturation on vulcanization appears in most examples to amount to only several units of percentage at the point of optimum vulcanization; but often chemical incorporation of sulfur continues beyond this point, and concurrently the unsaturation usually continues to decrease, although the amount of this decrease varies considerably from accelerator to accelerator. For sulfur used alone as vulcanizing agent, a larger decrease in unsaturation than the foregoing value was observed at the point of optimum vulcanization, and both the incorporation of sulfur and the decrease in unsaturation continued rapidly beyond this point. The best vulcanizates over the range of experiments were obtained when the proportion of combined sulfur at the point of optimum vulcanization amounted to approximately 2 atoms per double bond lost, and not to 1 atom, as has previously been supposed. It appears, therefore, from these observations that the incorporation of sulfur, and the concurrent saturation of double bonds can continue (especially if sulfur alone is used) after the essential work of vulcanization is completed, and this reactivity may perhaps be considered as a side reaction which, although having an effect on the properties of the vulcanizates, is subsidiary to the basic process of vulcanization.

Such subsidiary saturation of the double bonds could conceivably be caused by the direct addition of hydrogen sulfide, if sufficient of this reagent were generated in the vulcanization reaction (for which there is little direct evidence), or alternatively it might result from a secondary reaction following after the primary reaction at the α-methylene carbon atoms; on the other hand, it is quite unlikely, in view of the usual incapacity of sulfur to act as an addendum for olefins, to be caused by the direct addition of sulfur at the double bonds. The fact that sulfur reacts readily with unconjugated di- and polyolefinic substances such as linoleic and linolenic esters and glycerides (these substances show a marked tendency for the ordinary olefinic additivity to be replaced by an α-methylenic substitutive tendency) suggests that the initial attack by sulfur in the sulfur-vulcanization reaction may occur (like that of oxygen) at the α-methylene groups, and may possibly be succeeded (somewhat comparably with secondary autoxidation processes) by one or several types of secondary reaction which cause saturation of the double bonds. Such α-methylenic attack by sulfur may well be initiated by extraneous free radicals formed under vulcanization conditions, or possibly by free radicals formed by direct thermal dissociation of α-methylenic hydrogen atoms. The precise course of reaction, however, remains to be determined.

Another phenomenon which appears to involve the production of a vulcanized structure in which the incorporation of foreign atoms or fragments in the hydrocarbon chains plays a part is the photogelling of dissolved rubber. The absolute dependence of this phenomenon on sunlight or ultraviolet light, its entire independence of any concurrent autoxidation process[26], and also its promotion by acetone, acetophenone, benzophenone, etc., and by certain halogenated solvents (carbon tetrachloride, ethylene dibromide, chloroform, chloro- and dichlorobenzene, dichloro- and trichloroethylene, in order of decreasing efficiency) which not only are themselves prone to undergo photochemical decomposition with formation of free radicals, but can contribute these radicals (alkyl groups formed from the ketones, and chlorine atoms and chlorinated fragments from the halogenated solvents) to the interlinking hydrocarbon units or molecules, all suggest that the gelling takes a course closely analogous to those represented above for cyclohexene and benzoyl peroxide. Stevens[27] has described the progress of gelling with the above-mentioned and other promoters, one or more of these usually acting as solvents for the rubber. Mixtures of acetone and carbon tetrachloride are particularly effective as promoters, and ethyl ether containing peroxides or acting in the presence of such peroxides as barium peroxide is also successful. Benzoyl peroxide in carbon tetrachloride-acetone acts very slowly in the dark, but more effectively under illumination to give extensively chlorinated gels, thus suggesting that, although in general free-radical decomposition of peroxides promoted by light can initiate the gelling reaction, yet a slow thermal decomposition similar to that which occurs in Ostromislensky's reaction at 140° can also feebly initiate gelling in conjunction with carbon tetrachloride-acetone. The gels produced differ in consistency, according to the efficiency of the promoters used, from tenuous gels, which oxidize readily in the presence of air and light to regenerate liquids, to tough materials easily cut by scissors. The dried rubbers recovered from the gels by evaporation of the solvent differ correspondingly in physical properties, but the extent to which the gelling promoters have become incorporated is shown by the large increases in weight, and in the case of halogenated promoters by the substantial halogen contents, most of which remain after treatment of the materials by boiling alcoholic potash. As would be expected, the physical properties of the dried halogenated photogels obtained from rubber by means of benzoyl peroxide dissolved in carbon tetrachloride-acetone differ considerably from those of rubber vulcanized by Ostromislensky's procedure.

The profound difference between the result of irradiating rubber in presence of a potential source of free radicals such as acetaldehyde, first in strict absence of oxygen, and then in presence of oxygen, is clear from experiments of Spence and Ferry[28]. Under the first conditions, vulcanization or "polymerization" occurs in the manner described above, and in the second, rapid autoxidation of the rubber sets in, with oxidative scission of the hydrocarbon chains and "depolymerization" of the rubber. The acetaldehyde in the latter conditions acts as a powerful autoxidation catalyst[29].

SUMMARY

It is known that, when benzoyl peroxide is heated with rubber at 140°, interaction takes place and the rubber undergoes a species of vulcanization. To elucidate the course of this reaction, the behavior of benzoyl peroxide towards a typical olefin, cyclohexene, has been examined. Numerous products, including C_6- and C_{12}-hydrocarbons and benzoates of these, are formed, the

reaction involving thermal decomposition of the peroxide to give free phenyl and benzoate radicals. These radicals lead to (1) interlinking of the olefin molecules, and (2) formation of derivatives of both the simple and the "polymeric" olefins. The olefin molecules are attacked by the radicals principally at the α-methylene groups, but in part at the double bonds. The results described not only disclose an important reactivity of olefins, but afford an explanation of numerous vulcanization reactions which rubber undergoes, and also of certain photogelling reactions which are promoted by free-radical sources.

EXPERIMENTAL

Action of benzoyl peroxide on cyclohexene.—The peroxide (50 g.; 1 mol.) and cyclohexene (200 cc.; 9.6 mols.) were heated together in a stainless-steel autoclave or in sealed glass tubes at 140° for 6 hours. Carbon dioxide was produced, and caused a small increase above atmospheric pressure in the cooled vessel. The resulting clear, slightly yellow liquid was shaken several times with 2 *N* sodium hydroxide, then with water, and finally it was dried over anhydrous sodium sulfate. The combined alkaline and aqueous washings were acidified, and the precipitated acid was filtered off; it proved to be benzoic acid, m. p. 121° (equiv., 122), uncontaminated by any other acid.

The main reaction product was fractionally distilled: at atmospheric pressure, a forerun (I) (102 g.), consisting mainly of unchanged cyclohexene, passed over, leaving a liquid residue which was divided into the following fractions by distillation at 0.1 mm. pressure: (II) (*a*) b. p. 70—74° (7.2 g.), (*b*) 74—110° (1.0 g.); (III) (*a*) 112—116° (33 g.), (*b*) 116° (2.0 g.), (*c*) residue in still (16.8 g.). The distillates were colorless liquids, the earlier ones mobile, the later ones viscous liquids. The residue was divided by distillation from a molecular (batch) still into the fractions: (IV) (*a*) bath-temperature 146—148° (12.9 g.), (*b*) bath-temp. 150—180° (1.1 g.), (*c*) yellow, very viscous, oily residue (2.8 g.), probably somewhat decomposed. This procedure was carried out numerous times with new batches of the reactants, but in the later experiments the refractionation of fraction (IV) was omitted.

Fraction (I).—The forerun, although consisting mainly of cyclohexene, was not homogeneous. The likely adulterants were cyclohexane and benzene, but these were present in too small proportion to permit of their separation by careful fractional distillation, either directly, or after conversion of the cyclohexene component into its dibromide; indeed, no satisfactory method of demonstrating the presence of a little cyclohexane in the forerun was discovered. Spectroscopic examination, however, of the forerun showed unmistakably that a benzenoid compound was present. The absorption curves for (*a*) benzene in cyclohexane, and (*b*) cyclohexene in cyclohexane at dilutions of 2.5% and below show sufficiently marked differences to permit the presence of benzene to be distinguished at concentrations greater than 0.1%, and the presence of cyclohexene at concentrations above 2%. When both benzene and cyclohexene are present in cyclohexane, the former cannot be detected with certainty if the concentration of cyclohexene is above about 3%, and the latter cannot be detected if the concentration of the benzene exceeds 0.1%; consequently, unless the concentration of benzene in the mixture is less than 1/30 of that of the cyclohexene and itself exceeds 0.05%, its characteristic absorption will be masked by that due to the cyclohexene. The absorption curves for (1) dilute solutions of benzene and cyclohexene (together) in cyclohexane, and (2) dilute solutions of the forerun in cyclohexane were found to

be closely similar, but when solutions in cyclohexane of the hydrogenated forerun, *i.e.*, forerun which had been hydrogenated as fully as possible at room temperature in presence of Adams's catalyst to convert cyclohexene into cyclohexane, were examined, the presence of benzene became unmistakable, and its concentration in the forerun was estimated to be 2.5%.

Fraction (II) (*a*).—This fraction was an impure hydrocarbon of the C_{12}-series containing about 1% of oxygen and $\overline{\overline{1.74}}$ (found: C, 88.05, 87.9, 88.15; H, 10.95, 11.05, 10.95; iodine value, 272. Calculated for $C_{12}H_{18}$: C, 88.8; H, 11.2%; iodine value, 313).

A portion of this fraction (1 g.) was heated with powdered selenium (2 g.) at about 300° for 100 hours. The product was extracted with ether, the ether distilled, and the oily residue heated for a time over sodium. The liquid residue was freed from a little solid inorganic matter by dissolving it in ether, filtering, and removing the solvent; afterwards it was distilled. The bulk (0.5 g.) distilled at 98—108°/12 mm., and appeared to be unchanged hydrocarbon, but the succeeding portion distilled when the bath reached 200°, and solidified in the receiver. This solid was biphenyl, m. p. 69° (mixed m. p. 68—69°) (found: C, 93.1; H, 6.75. Calculated for $C_{12}H_{10}$: C, 93.5; H, 6.5%).

Hydrogenation of a portion (4.7 g.) of this fraction in 5 cc. of alcohol at room temperature and pressure in presence of Raney nickel (1240 cc. of hydrogen absorbed, corresponding to 95.4% of that required for $C_{12}H_{18}$) gave a colorless liquid hydrocarbon, saturated to alkaline permanganate, but having too high a C/H ratio for cyclohexylcyclohexane (found: C, 87.3, 87.15; H, 12.75, 12.75. Calculated for $C_{12}H_{22}$: C, 86.65; H, 13.35%). Spectroscopic examination of the hydrogenated hydrocarbon side by side with pure cyclohexylcyclohexane revealed U.V. absorption for the former approximately 100 times as strong as was shown by the latter, and an absorption band for the former in the appropriate region for benzene derivatives (2400—2550 A.; $\log_m \xi = 2.0$); no individual maxima could, however, be observed. The curve for the hydrogenated hydrocarbon was approximately a mean between those of cyclohexylcyclohexane and biphenyl, but it has not been possible to make direct comparison with the curve for pure phenylcyclohexane. The succeeding experiments confirm that the bulk of fraction (II) (*a*) was cyclohexenylcyclohexene; the contaminant was doubtless mainly phenylcyclohexene, with possibly a little phenylcyclohexane.

A further portion of fraction (II) (*a*) (9 g.) was dissolved in chloroform and treated gradually at 0° with excess of 0.2 *N* bromine in chloroform (2 mols. of Br_2 per mol. of $C_{12}H_{18}$). The excess of bromine and most of the chloroform were evaporated at reduced pressure, whereupon much crystalline bromide separated (65% yield). This formed colorless prisms, m. p. 159°, from chloroform and proved to be $\Delta^{2'}$-cyclohexenyl-Δ^{2}-cyclohexene tetrabromide (found: C, 29.8, 29.9; H, 3.9, 4.05; Br, 66.25. $C_{12}H_{18}Br_4$ requires C, 29.9; H, 3.75; Br, 66.35%). The tetrabromide appears to be identical with that, m. p. 158°, obtained by Cogan and Marvel[30] from a hydrocarbon which they thought was probably di-Δ^{2}-cyclohexenyl.

A portion of the tetrabromide (9 g.) was debrominated by zinc dust in alcoholic solution, giving thereby the parent hydrocarbon $\Delta^{2'}$-cyclohexenyl-Δ^{2}-cyclohexene, but this was contaminated with a little bromide (found: C, 86.3; H, 10.6%). The constitution of the hydrocarbon was established by ozonization of a portion in chloroform, without further purification, the ozonide giving on decomposition with water, and further oxidation of the product with dilute alkaline permanganate at 0°, a tetracarboxylic acid, $C_8H_{14}(CO_2H)_4$, which sepa-

rated from ether (in which it was sparingly soluble) as a white crystalline powder, m. p. 177°. This was *n*-octane-$\alpha\delta\epsilon\theta$-tetracarboxylic acid (found: C, 49.8; H, 6.45; equiv., 72.3. $C_{12}H_{18}O_8$ requires C, 49.65; H, 6.25%; equiv., 72.5).

The bromide recovered from the mother liquors was freed as far as possible from the crystalline bromide by crystallization of the latter from light petroleum, and the solvent then completely removed at reduced pressure. The residual bromide was a brown viscous liquid (found: Br, 59.3%). To remove from this any unbrominated (nonolefinic) hydrocarbons of the C_{12}-series, the liquid bromide was partly distilled at 0.05 mm. pressure, whereupon only a few drops (0.1 g.) of impure hydrocarbon (found: C, 81.05; H, 9.05%) passed over, leaving a residue which from its bromine content appeared to consist largely of a dibromide. This was probably, in view of the foregoing spectroscopic evidence, derived from phenylcyclohexene; some proportion of the dibromide of cyclohexylcyclohexene may, however, have been present.

Fraction (II) (*b*).—This consisted of a mixture of C_{12} hydrocarbon and the material of fraction (III).

Fraction (III) (*a*).—This colorless oil of strong odor consisted of a mixture of benzoates of C_6 alcohols. The analytical values, which differed little from preparation to preparation, taken in conjunction with the iodine and benzoyl values, show that the mixture consisted of cyclohexenyl benzoate and cyclohexyl benzoate in roughly the proportion of 3 : 10 (found: C, 76.55; H, 7.65; Bz, 59.4; iodine value, 38.4. Calculated for $C_6H_5CO_2C_6H_9$: C, 77.3; H, 6.9; Bz, 60.0%; iodine value, 125. Calculated for $C_6H_5CO_2C_6H_{11}$: C, 76.5; H, 7.85; Bz, 59.4%; iodine value, 0). The benzoyl value was determined by refluxing portions (6 g.) of the mixed esters with *N* methyl-alcoholic sodium hydroxide (100 cc.) in nitrogen for 5 hours, and then titrating with *N* hydrochloric acid.

The mixed alcohols from the hydrolyzed ester fraction were obtained by distilling off, through a column, the methyl alcohol from the basified hydrolysis products, and then thoroughly extracting the residue with ether. The ethereal solution after being dried (anhydrous sodium sulfate), gave a colorless, viscous liquid of strong smell. This was a mixture (*ca.* 1 : 4) of cyclohexen-3-ol and cyclohexanol (found: C, 72.35; H, 11.65; iodine value, 64; calculated for $C_6H_{10}O$: C, 73.4; H, 10.3%; iodine value, 258.8; calculated for $C_6H_{12}O$: C, 71.9; H, 12.1%). A crude α-naphthylurethane prepared from the mixture gave, after several crystallizations from ether, the pure α-naphthylurethane of cyclohexanol, forming colorless needles, m. p. 128° (mixed m. p. 128°) (found: C, 76.0; H, 6.8; N, 5.4; calculated for $C_{17}H_{19}O_2N$: C, 75.8; H, 7.1; N, 5.2%); the corresponding derivative of cyclohexen-3-ol was not isolated in pure form. Acidification of the alkaline hydrolysis liquor gave at once benzoic acid, which melted, after one recrystallization from water, at 121°; no other aromatic acid could be found.

On addition of 0.2 *N* bromine in chloroform to a solution of the mixed alcohols (0.8 g.) in chloroform at 0°, 0.3 mol. of bromine was decolorized, and the product gave, on removal of the solvent at reduced pressure, a liquid from which by distillation (1) 0.5 g. of crystallizable cyclohexanol, b. p. 60—64°/12 mm., and (2) 0.5 g. of 1 : 2-dibromocyclohexan-3-ol (clusters of needles, m. p. 55°, from light petroleum; mixed m. p. with authentic specimen of m. p. 55°, 55°; found: C, 27.8; H, 4.2; Br, 62.4; calculated for $C_6H_{10}OBr_2$: C, 27.9; H, 3.9; Br, 62.0%) were isolated.

Fraction (IV).—The subfractions (*a*)—(*e*) were entirely saponifiable. Each fraction was analyzed and then hydrolyzed by 5 hours' heating with *N* methyl-

alcoholic sodium hydroxide. The derived alcohols were also analyzed. It was apparent that no satisfactory fractionation had been achieved. A much better result was obtained by hydrolyzing batches of fraction (IV) directly, *i.e.*, without any distillation, and isolating and fractionally distilling the derived alcoholic material at *ca.* 0.3 mm. pressure. Numerous such fractions were obtained, having somewhat different compositions and unsaturations, but the bulk of the material fell into three rather well-defined fractions: (1) a small amount of mobile liquid, b. p. 80°/0.3 mm., (2) a viscous liquid, b. p. 90—100°/0.5 mm., (3) a very viscous liquid, b. p. 100—118°/0.1 mm. The subfraction (1) resembled in all characteristics the mixture of cyclohexanol and cyclohexenol obtained by hydrolysis of fraction (III), and was not further examined. The subfraction (2) was a monoölefinic dicyclic alcohol, $C_{12}H_{20}O$ (found: C, 80.2; H, 11.15; iodine value, 112[31]; *M* (in benzene), 185; calculated for $C_{12}H_{20}O$: C, 79.9; H, 11.1%; iodine value, 141; *M*, 180). This probably consisted mainly of Δ^2-cyclohexenylcyclohexan-2-ol, although some proportion of its isomeride, 1-cyclohexyl-Δ^2-cyclohexen-4-ol, may have been present. The subfraction (3), which distilled only with difficulty at 0.1 mm., gave carbon and molecular-weight values well above those required for a dicyclic alcohol of the C_{12} series. The composition varied somewhat from preparation to preparation (*e.g.*, found: (1) C, 83.5; H, 11.6; *M*, 206; (2) C, 84.0; H, 10.7; *M*, 214; (3) C, 82.8; H, 10.8%), but the range of variation in the hydrogen values was comparatively small. The fraction appeared to consist of a mixture of the dicyclic alcohols appearing in fraction (2), with a minor proportion of a tricyclic hydrocarbon such as phenylcyclohexylcyclohexane (calculated: C, 89.2; H, 10.8%; *M*, 242.2) or phenylcyclohexylcyclohexene (calculated: C, 89.9; H, 10.1%; *M*, 240.2).

The acid obtained by saponification of fraction (IV) was homogeneous benzoic acid.

Yields.—The following table shows approximately the recovery of PhCOO— groups (contained originally in the benzoyl peroxide) in a typical run employing 100 g. of peroxide and 400 cc. of cyclohexene.

Fraction	Weight (g.)	Weight of PhCOO— (g.)
(I) Forerun	—	—
(II) C_{12} hydrocarbon	24	(*ca.*) 2
(III) Benzoates of C_6 alcohol	51	30—32
(IV) Benzoates of C_{12} alcohol	31	12—13
Free benzoic acid	15	12—15
		Total 54—62

This shows that between 38 and 46 per cent by weight of the original PhCOO— groups in the peroxide had broken down during reaction, and must thus have given rise to phenyl radicals and carbon dioxide amounting to 12—14 and 7—8 per cent, respectively, of the weight of the original peroxide.

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STATISTICAL LENGTHS OF RUBBERLIKE HYDROCARBON MOLECULES *

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INTRODUCTION

It has been known for some time that the pure hydrocarbons of balata (or gutta-percha) and natural rubber have the same chemical composition and chemical properties[1]. Both balata and rubber appear to be polymers of isoprene, $(C_5H_8)_n$, with the same degree of unsaturation. Their physical properties are sufficiently different, however, to make it clear that their structures must differ in some important respect. Since the molecules contain numerous double bonds, it has been suggested that rubber and balata are geometric isomers.

Every fourth bond in a rubber or balata molecule is a double bond, so it follows that the possibilities for geometric isomerism are considerable. It was proposed by Meyer and Mark[2] that natural rubber hydrocarbon has a structure for which the molecular chain is *cis* with respect to all of the double bonds. Balata (or gutta-percha) is then supposed to have a *trans*-structure throughout, this view having been verified by Fuller[3] and Bunn[4]. It is the purpose of the present paper to consider, from the point of view of recent theories of rubber elasticity[5], to what extent these structures explain the differences in physical properties. The method to be employed involves calculation of the root mean square lengths of the *cis*- and *trans*-structures, which, when compared to their maximum lengths, should give an indication of their extensibilities.

In 1932 Eyring[6] treated the problem of the average square length of a hydrocarbon chain. In the present paper a different derivation of Eyring's equation is given (for illustrative purposes), after which this derivation will be extended to the rubberlike molecules with double bonds.

SATURATED HYDROCARBON CHAIN

Consider an unbranched hydrocarbon chain containing n carbon-carbon bonds, each of length σ and each making an angle α with the extension of an adjacent bond (Figure 1). Let us represent the bonds by vectors, $\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, \boldsymbol{\sigma}_3, \cdots, \boldsymbol{\sigma}_n$, and let $\mathbf{R}_n$ be the vector joining the first and last carbon atoms. Then

$$\mathbf{R}_n = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_3 + \cdots \boldsymbol{\sigma}_n. \tag{1}$$

From (1) it follows that

$$\begin{aligned}\mathbf{R}_n^2 = \boldsymbol{\sigma}_1^2 + \boldsymbol{\sigma}_2^2 + \boldsymbol{\sigma}_3^2 + \cdots \boldsymbol{\sigma}_n^2 + 2(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_2\cdot\boldsymbol{\sigma}_3 + \cdots \boldsymbol{\sigma}_{n-1}\cdot\boldsymbol{\sigma}_n) \\ + 2(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_3 + \boldsymbol{\sigma}_2\cdot\boldsymbol{\sigma}_4 + \cdots \boldsymbol{\sigma}_{n-2}\cdot\boldsymbol{\sigma}_n) + \cdots \\ + 2(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_{n-1} + \boldsymbol{\sigma}_2\cdot\boldsymbol{\sigma}_n) + 2(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_n).\end{aligned} \tag{2}$$

But

$$\boldsymbol{\sigma}_1^2 = \boldsymbol{\sigma}_2^2 = \boldsymbol{\sigma}_3^2 = \cdots \boldsymbol{\sigma}_n^2 = \sigma^2 \tag{3}$$

and

$$\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2 = \boldsymbol{\sigma}_2\cdot\boldsymbol{\sigma}_3 = \cdots = \boldsymbol{\sigma}_{n-1}\cdot\boldsymbol{\sigma}_n = \sigma^2 \cos\alpha. \tag{4}$$

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Moreover, if there is perfectly free rotation about the various bonds, then

$$\langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_{1+j} \rangle_{Av} = \langle \boldsymbol{\sigma}_2 \cdot \boldsymbol{\sigma}_{2+j} \rangle_{Av} = \cdots \langle \boldsymbol{\sigma}_{n-j} \cdot \boldsymbol{\sigma}_n \rangle_{Av}. \tag{5}$$

Letting R_n equal the root mean square length, we have

$$R_n^2 = \langle \mathbf{R}_n^2 \rangle_{Av} = n\sigma^2 + 2(n-1)\sigma^2 \cos\alpha + 2(n-2)\langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_3 \rangle_{Av} + 2(n-3)\langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_4 \rangle_{Av} + \cdots 2\langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_n \rangle_{Av}. \tag{6}$$

To evaluate $\langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_{1+j} \rangle_{Av}$ note that the component of $\boldsymbol{\sigma}_{1+j}$ on $\boldsymbol{\sigma}_j$ is $\sigma \cos\alpha$. Similarly the average component of $\boldsymbol{\sigma}_{1+j}$ on $\boldsymbol{\sigma}_{j-1}$ is $\sigma \cos^2\alpha$, etc. Hence

$$\langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_{1+j} \rangle_{Av} = \sigma^2 \cos^j \alpha \tag{7}$$

and

$$R_n^2 = n\sigma^2 + 2(n-1)\sigma^2 \cos\alpha + 2(n-2)\sigma^2 \cos^2\alpha + \cdots 2\sigma^2 \cos^{n-1}\alpha. \tag{8}$$

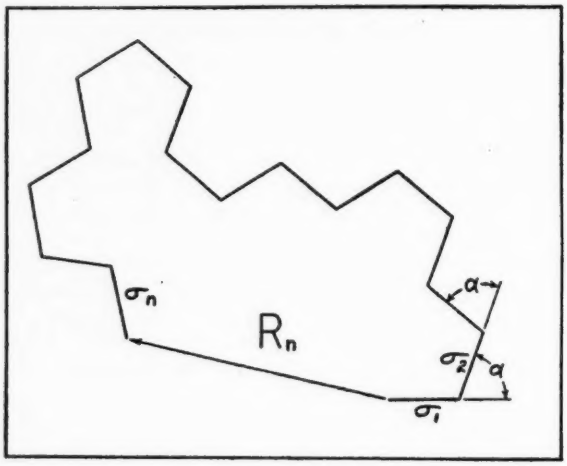

FIG. 1.—Saturated hydrocarbon chain.

By rearranging (8) there is obtained:

$$\frac{1}{n\sigma^2} R_n^2 = \frac{1+\cos\alpha}{1-\cos\alpha} - \frac{2\cos\alpha}{n}\left\{\frac{1-\cos^n\alpha}{(1-\cos\alpha)^2}\right\}. \tag{9}$$

If n is large, Equation (9) can be replaced by the approximate equation:

$$(1/n\sigma^2)R_n^2 = (1+\cos\alpha)/(1-\cos\alpha). \tag{10}$$

This was used by Guth and James[5] and others in connection with the statistical theory of rubber elasticity.

RUBBERLIKE MOLECULES

The derivation above will now be generalized and applied to molecules of the rubber type. Three cases will be considered: first, it will be assumed that the chain is *trans* throughout; next, it will be supposed that the chain is *cis*; and finally, it will be imagined that it is sometimes *trans* and sometimes *cis* in a perfectly random way.

Let the molecular chain under consideration be made up of n vectors $\boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, \boldsymbol{\sigma}_3, \boldsymbol{\rho}_4, \cdots$, where the $\boldsymbol{\sigma}$'s refer to single bonds and the $\boldsymbol{\rho}$'s to double bonds (Figure 2). Once more let α be the angle between a single bond and the extension of an adjacent single bond, and let β be the angle between a double bond and the extension of an adjacent (single) bond. Let $\mathbf{R}_n$ be the vector joining the first and last carbon atoms of the chain. Then

$$\mathbf{R}_n = \boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_3 + \boldsymbol{\rho}_4 + \boldsymbol{\sigma}_5 + \cdots \tag{11}$$

and

$$\begin{aligned}\mathbf{R}_n^2 = {} & \boldsymbol{\sigma}_1^2 + \boldsymbol{\sigma}_2^2 + \boldsymbol{\sigma}_3^2 + \boldsymbol{\rho}_4^2 + \boldsymbol{\sigma}_5^2 + \cdots \\ & + 2(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_2\cdot\boldsymbol{\sigma}_3 + \boldsymbol{\sigma}_3\cdot\boldsymbol{\rho}_4 + \boldsymbol{\rho}_4\cdot\boldsymbol{\sigma}_5 + \cdots) \\ & + 2(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_3 + \boldsymbol{\sigma}_2\cdot\boldsymbol{\rho}_4 + \boldsymbol{\sigma}_3\cdot\boldsymbol{\sigma}_5 + \boldsymbol{\rho}_4\cdot\boldsymbol{\sigma}_6 + \cdots) \\ & + 2(\boldsymbol{\sigma}_1\cdot\boldsymbol{\rho}_4 + \boldsymbol{\sigma}_2\cdot\boldsymbol{\sigma}_5 + \boldsymbol{\sigma}_3\cdot\boldsymbol{\sigma}_6 + \boldsymbol{\rho}_4\cdot\boldsymbol{\sigma}_7 + \cdots) \\ & + 2(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_5 + \boldsymbol{\sigma}_2\cdot\boldsymbol{\sigma}_6 + \boldsymbol{\sigma}_3\cdot\boldsymbol{\sigma}_7 + \boldsymbol{\rho}_4\cdot\boldsymbol{\rho}_8 + \cdots) + \cdots.\end{aligned} \tag{12}$$

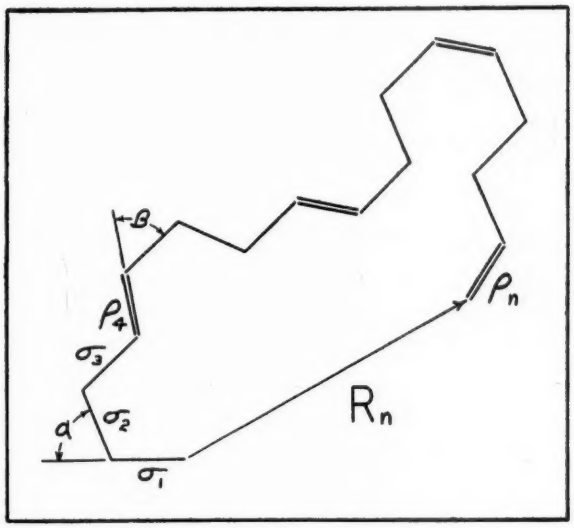

FIG. 2.—Random rubberlike molecular chain.

It is readily seen from the model that many of the products which appear in (12) are equivalent, for example:

$$\begin{aligned}\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2 &= \boldsymbol{\sigma}_2\cdot\boldsymbol{\sigma}_3 = \boldsymbol{\sigma}_5\cdot\boldsymbol{\sigma}_6 = \cdots \\ \langle\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_3\rangle_{Av} &= \langle\boldsymbol{\sigma}_5\cdot\boldsymbol{\sigma}_7\rangle_{Av} = \cdots, \\ \boldsymbol{\sigma}_3\cdot\boldsymbol{\rho}_4 &= \boldsymbol{\rho}_4\cdot\boldsymbol{\sigma}_5 = \boldsymbol{\sigma}_7\cdot\boldsymbol{\rho}_8 = \cdots, \quad \text{etc.}\end{aligned} \tag{13}$$

Introducing relationships (13) into (12), and making an approximation equivalent to going from Equation (9) to Equation (10), there is obtained the following approximate equation valid for large values of n:

$$\begin{aligned}\frac{1}{n}R_n^2 = {} & \tfrac{3}{4}\sigma^2 + \tfrac{1}{4}\rho^2 + (\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2 + \boldsymbol{\sigma}_3\cdot\boldsymbol{\rho}_4) \\ & + \tfrac{1}{2}(\langle\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_3\rangle_{Av} + 2\langle\boldsymbol{\sigma}_2\cdot\boldsymbol{\rho}_4\rangle_{Av} + \langle\boldsymbol{\sigma}_3\cdot\boldsymbol{\sigma}_5\rangle_{Av}) + (\langle\boldsymbol{\sigma}_1\cdot\boldsymbol{\rho}_4\rangle_{Av} + \langle\boldsymbol{\sigma}_2\cdot\boldsymbol{\sigma}_5\rangle_{Av}) \\ & + \tfrac{1}{2}(3\langle\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_5\rangle_{Av} + \langle\boldsymbol{\rho}_4\cdot\boldsymbol{\rho}_8\rangle_{Av}) + (\langle\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_6\rangle_{Av} + \langle\boldsymbol{\sigma}_3\cdot\boldsymbol{\rho}_8\rangle_{Av}) + \cdots.\end{aligned} \tag{14}$$

But by a generalization of the method used for the hydrocarbon chain, it is seen that

$$\begin{aligned} \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 &= \sigma^2 \cos \alpha, \\ \boldsymbol{\sigma}_3 \cdot \boldsymbol{\varrho}_4 &= \sigma\rho \cos \beta, \\ \langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_3 \rangle_{Av} &= \sigma^2 \cos^2 \alpha, \\ \langle \boldsymbol{\sigma}_2 \cdot \boldsymbol{\varrho}_4 \rangle_{Av} &= \sigma\rho \cos \alpha \cos \beta, \\ \langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\varrho}_4 \rangle_{Av} &= \sigma\rho \cos^2 \alpha \cos \beta, \end{aligned} \tag{15}$$

and

$$\langle \boldsymbol{\varrho}_4 \cdot \boldsymbol{\varrho}_8 \rangle_{Av} = \rho^2 \cos^2 \alpha \cos^2 \beta.$$

Equations (15) are true whether the chain is *cis*, *trans*, or random. The other averages which appear in (14) depend on the nature of the chain and are given by expressions of the following type:

$$\begin{aligned} \langle \boldsymbol{\sigma}_3 \cdot \boldsymbol{\sigma}_5 \rangle_{Av} &= \sigma^2 && (trans) \\ &= \sigma^2 \cos 2\beta && (cis) \\ &= \sigma^2 \cos^2 \beta, && (\text{random}) \\ \langle \boldsymbol{\sigma}_2 \cdot \boldsymbol{\sigma}_5 \rangle_{Av} &= \sigma^2 \cos \alpha && (trans) \\ &= \sigma^2 \cos \alpha \cos 2\beta && (cis) \\ &= \sigma^2 \cos \alpha \cos^2 \beta, && (\text{random}) \\ \langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_5 \rangle_{Av} &= \sigma^2 \cos^2 \alpha && (trans) \\ &= \sigma^2 \cos^2 \alpha \cos 2\beta && (cis) \\ &= \sigma^2 \cos^2 \alpha \cos^2 \beta. && (\text{random}) \end{aligned} \tag{16}$$

Moreover, for terms like $\langle \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_6 \rangle_{Av}$ and higher terms, it is seen that

$$\begin{aligned} \langle \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_{j+4} \rangle_{Av} &= \langle \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j \rangle_{Av} \cos^2 \alpha && (trans) \\ (j \gtrless i) &= \langle \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j \rangle_{Av} \cos^2 \alpha \cos 2\beta && (cis) \\ &= \langle \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j \rangle_{Av} \cos^2 \alpha \cos^2 \beta, && (\text{random}) \\ \langle \boldsymbol{\sigma}_i \cdot \boldsymbol{\varrho}_{j+4} \rangle_{Av} &= \langle \boldsymbol{\sigma}_i \cdot \boldsymbol{\varrho}_j \rangle_{Av} \cos^2 \alpha && (trans) \\ (j > i) &= \langle \boldsymbol{\sigma}_i \cdot \boldsymbol{\varrho}_j \rangle_{Av} \cos^2 \alpha \cos 2\beta && (cis) \\ &= \langle \boldsymbol{\sigma}_i \cdot \boldsymbol{\varrho}_j \rangle_{Av} \cos^2 \alpha \cos^2 \beta, && (\text{random}) \\ \langle \boldsymbol{\varrho}_i \cdot \boldsymbol{\varrho}_{j+4} \rangle_{Av} &= \langle \boldsymbol{\varrho}_i \cdot \boldsymbol{\varrho}_j \rangle_{Av} \cos^2 \alpha && (trans) \\ (j > i) &= \langle \boldsymbol{\varrho}_i \cdot \boldsymbol{\varrho}_j \rangle_{Av} \cos^2 \alpha \cos 2\beta && (cis) \\ &= \langle \boldsymbol{\varrho}_i \cdot \boldsymbol{\varrho}_j \rangle_{Av} \cos^2 \alpha \cos^2 \beta. && (\text{random}) \end{aligned} \tag{17}$$

Introducing (15), (16), and (17) into (13), it is possible to evaluate $(1/n)R_n^2$ for the different kinds of chains. By simplification and rearrangement, the following expressions are obtained. For the *trans*-structure:

$$\frac{1}{n} R_n^2 = \rho^2 \left\{ \frac{1 + \cos^2 \alpha \cos 2\beta}{4(1 - \cos^2 \alpha)} \right\} + \rho\sigma \left\{ \frac{\cos \beta (1 + \cos \alpha + \cos^2 \alpha)}{1 - \cos^2 \alpha} \right\} + \sigma^2 \left\{ \frac{5 + 8 \cos \alpha + 5 \cos^2 \alpha}{4(1 - \cos^2 \alpha)} \right\}. \tag{18}$$

For the *cis*-structure:

$$\frac{1}{n} R_n^2 = \rho^2 \left\{ \frac{1 + \cos^2 \alpha}{4(1 - \cos^2 \alpha \cos 2\beta)} \right\} + \rho\sigma \left\{ \frac{\cos \beta (1 + \cos \alpha + \cos^2 \alpha)}{1 - \cos^2 \alpha \cos 2\beta} \right\} + \sigma^2 \left\{ \frac{(3 + 2 \cos 2\beta) + 4 \cos \alpha (1 + \cos 2\beta) + \cos^2 \alpha (2 + 3 \cos 2\beta)}{4(1 - \cos^2 \alpha \cos 2\beta)} \right\}. \tag{19}$$

For the random structure:

$$\frac{1}{n}R_n^2 = \rho^2\left\{\frac{1+\cos^2\alpha\cos^2\beta}{4(1-\cos^2\alpha\cos^2\beta)}\right\} + \rho\sigma\left\{\frac{\cos\beta(1+\cos\alpha+\cos^2\alpha)}{1-\cos^2\alpha\cos^2\beta}\right\}$$
$$+\sigma^2\left\{\frac{(3+2\cos^2\beta)+4\cos\alpha(1+\cos^2\beta)+\cos^2\alpha(2+3\cos^2\beta)}{4(1-\cos^2\alpha\cos^2\beta)}\right\}. \quad (20)$$

NUMERICAL CALCULATIONS

To obtain numerical values for the average square lengths of the different rubberlike molecules, it is necessary to assume definite values for α, β, ρ, and σ. Using the values of Brockway and coworkers[7], the angles are taken to be $\alpha = 68° 30'$ and $\beta = 55° 40'$. These values were obtained by electron diffraction methods applied to small molecules, and it is assumed that they are valid for polymers as well. These figures differ slightly from the experimental values obtained for crystalline rubberlike materials[4], but it is supposed here that the noncrystalline rubberlike molecules have angles close to those for small gaseous molecules. For σ and ρ, Pauling's values[8] for the single and double carbon-carbon bond distances will be used. These are $\sigma = 1.54$A and $\rho = 1.34$A.

For the root mean square lengths of the molecules, numerical calculations using Equations (18), (19), and (20) yield the following results:

$$R_n = 2.90\sqrt{n}\text{ A}, \quad (\textit{trans})$$
$$R_n = 2.01\sqrt{n}\text{ A}, \quad (\textit{cis})$$
$$R_n = 2.45\sqrt{n}\text{ A}. \quad (\text{random})$$

It follows from the above figures that a *trans*-molecule is, on the average, 44 per cent longer than a *cis*-molecule, provided that both have the same number of members in their respective chains. The average length of a random molecule is just about half-way between those of the *cis*- and *trans*-varieties.

Since a *cis*-molecule tends to be more curled up than a *trans*-molecule, it might be expected that a mass of *cis*-molecules would be capable of greater stretching than a mass of *trans*-molecules. This is in qualitative agreement with the fact that natural rubber can be stretched more than balata. Since some varieties of synthetic rubbers may be random, they would be expected to possess intermediate elastic properties.

MAXIMUM LENGTHS OF MOLECULES

For a quantitative measure of the elastic possibilities, it is necessary to consider still another factor. The average lengths of the molecules (which are nearly the same as the root mean square lengths) must be compared with the maximum possible lengths. Since the maximum length of a *trans*-molecule is greater than the maximum length of a *cis*-molecule, it is conceivable that an average *trans*-molecule may undergo as great a relative stretch as one of the *cis*-variety. To check this possibility, we shall calculate the maximum possible lengths for the two forms.

In Figure 3 are pictured the two regular varieties of rubberlike polymers arranged in such a way as to make the maximum lengths. By purely geometric considerations, it is seen that for the *trans*-variety:

$$R_{n(\max)} = \frac{n}{4}\{\rho^2 + 2\rho\sigma[2\cos\beta + \cos(\beta-\alpha)] + 5\sigma^2 + 4\sigma^2\cos\alpha\}^{\frac{1}{2}} \quad (21)$$

and for the *cis*-form:

$$R_{n(\max)} = \frac{n}{4}\{\rho + 2\sigma\cos\beta + \sigma\cos(\beta - \alpha)\}. \qquad (22)$$

In deriving (21) and (22), it is assumed that the molecules are long and made up of recurring units each containing one double and three single bonds.

Performing the necessary numerical calculations, using the same values for α, β, ρ, and σ as before, it is found that

$$R_{n(\max)} = 1.27n \text{ A} \quad (trans)$$

and

$$R_{n(\max)} = 1.14n \text{ A}. \quad (cis)$$

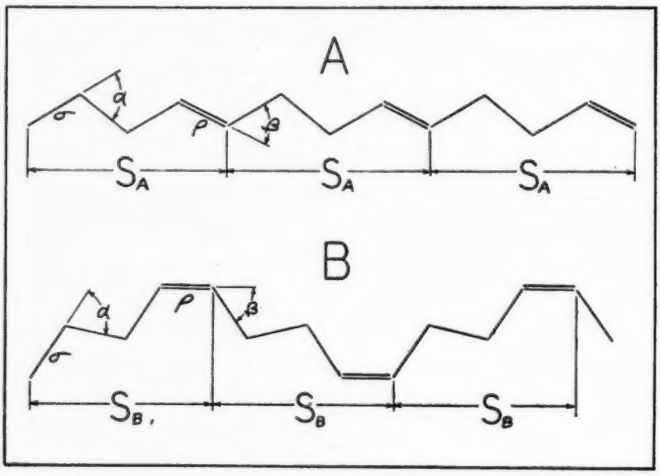

FIG. 3.—Rubberlike molecules arranged for maximum length. A. *Trans*-variety. B. *Cis*-variety. In each case $R_{n(\max)} = (n/4)S$.

The quantity of significance for our purpose is the ratio of $R_{n(\max)}$ to R_n, which provides a measure of the elastic possibilities. These ratios are for the *trans*- and *cis*-varieties, and are equal, respectively, to $0.438\sqrt{n}$ and $0.567\sqrt{n}$. Moreover, the ratio for the *cis*-variety is 1.30 times as great as that for the *trans*.

DISCUSSION

On the basis of the molecular picture of rubber elasticity[5], the figure 1.30 may be interpreted in the following way. Take two pieces of *cis*- and *trans*-material of the same size and shape, made up of molecules of the same chain length. Let each be stretched until it reaches some characteristic place in the stress-strain curve or reaches some particular state of crystallization. Then the *cis*-material should be 30 per cent longer than the *trans*-material. In other words, if 100 per cent elongation should cause crystallization for the *trans*-substance, then 160 per cent elongation should be necessary for the corresponding effect in the *cis*-substance. (Incidentally, small changes in α, β, ρ, or σ do not alter the above ratios appreciably.)

Qualitatively the argument advanced above is in the right direction as far as rubber and balata are concerned. Unfortunately, the difference predicted

is not nearly great enough, especially at room temperature, under which condition balata is scarcely elastic at all. A better comparison is obtained between polychloroprene and natural rubber. Polychloroprene has a *trans*-structure[9], yet possesses considerable elasticity. No accurate experimental data are available for comparing samples of polychloroprene and natural rubber of the same molecular weight and in the same state of vulcanization, but there appears to be qualitative evidence in support of the above arguments.

To account fully for the different elastic properties of the various rubberlike polymers, it is necessary to take into account other effects, such as those suggested by Bunn[10]. Bunn recognized that steric influences of different substituents (CH_3 or Cl) in the polymer chains have an important effect on the curling of molecules. Such steric effects become of major importance in balata, thus accounting for its nonelastic properties at room temperature. For natural rubber, the structure is such that the effect of the methyl group is not important, and for polychloroprene the dimensions are such that the steric effect is rendered small. The present calculation, although inadequate as a complete explanation, does indicate to what extent the chain structure without substituents affects the elastic properties of polymers.

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THE CRYSTAL STRUCTURE OF β-ISOPRENE SULFONE *

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A detailed x-ray analysis has shown that the molecule of β-isoprene sulfone has a heterocyclic structure in which resonance occurs between the three carbon-carbon bonds of the C_4S ring. The bond lengths are C—C (in the ring) 1.41 A., C (ring)—C (methyl) 1.54 A., C—S 1.75 A., and S—O 1.44 A., all ± 0.02 A.; the distribution of the four sulfur bonds is approximately tetrahedal.

It is not possible to determine the structure of crystalline rubber uniquely and exactly from the data of x-ray fibre diagrams alone. These data must, therefore, be very largely supplemented in other ways by accurate information from which the bond lengths and valency angles in the primary polyisoprene chain and the probable relative disposition of atoms in neighboring chains can be inferred.

To obtain this information, it is proposed to make a systematic study of the crystal structures of relatively simple compounds containing isoprene units or atomic groupings related to isoprene, and the present paper contains the results of the first investigation of this series, on β-isoprene sulfone. This substance was chosen because the presence of the relatively heavy sulfur atom made it possible to carry out a detailed and accurate analysis without undue labor, and because, in view of the technical importance of vulcanization, it was desirable to investigate a simple system containing sulfur attached to an isoprene unit. It was also hoped to establish the structure of this sulfone entirely independently of purely chemical evidence, on account of its importance as a representative of a large class of compounds of sulfur dioxide with conjugated dienes.

By crystallographic examination of β-isoprene sulfone, Sauter[1] gave for the cell dimensions: $a = 6.60$, $b = 7.62$ and $c = 6.67$ A.; $\beta = 110° 34'$, and reported the space-group as $P2_1$. Our independent measurements of the unit cell are: $a = 6.77$, $b = 7.72$, $c = 6.70$ A., $\beta = 110° 42'$.

There are two molecules of $C_5H_8O_2S$ in the unit cell. The only systematic extinctions are (*oko*) absent for k odd, so that the space-group may be either $P2_1$ or $P2_1/m$. The results of the F^2 syntheses (see below) strongly suggested the latter, and this was assumed for the subsequent F syntheses. The final result fully substantiated this assumption.

The structure amplitudes of 454 planes were obtained experimentally from relative intensity measurements on oscillation photographs taken about the principle axes, coupled with absolute intensity measurements on selected planes. These amplitudes were used to carry out three dimensional F^2 (Patterson) Fourier syntheses for $y = 0$ and $y = 1/2$, the appropriate formulae being:

$$P_{xoz} = 4 \sum_{-H}^{H} \sum_{0}^{L} [\sum_{0}^{K} F^2_{hkl}] \cos 2\pi(hx + lz).$$

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and

$$P_{xyz} = 4 \sum_{-H}^{H} \sum_{0}^{L} [\sum_{0}^{K} F^2_{hkl}(-1)^k] \cos 2\pi(hx + lz).$$

These summations and the subsequent F-syntheses were effected by the method of Beevers and Lipson[2]; the results are shown in Figures 1 and 2 with skeleton molecular formulas superimposed.

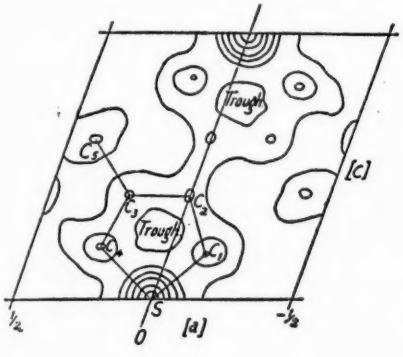


FIG. 1

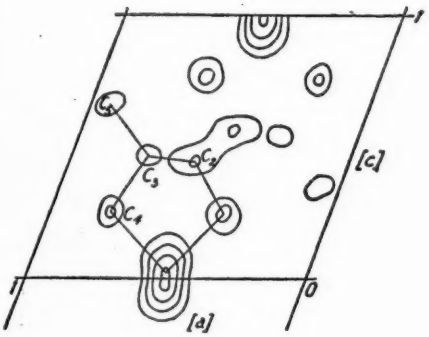


FIG. 2

The height of a peak in an F^2 synthesis is determined approximately by the product of the atomic numbers of the two atoms which give rise to the peak; in the present case, therefore, it is to be expected that the S—S peaks will be outstanding, and that the C—C peaks will probably be negligible by comparison with S—C and S—O peaks.

Owing to the presence of a two-fold screw axis of symmetry, the S—S peaks must occur in the F^2 synthesis at $y = 1/2$, and they can be identified without difficulty in Figure 2. Apart from the large peak at the origin in Figure 1 (which is merely an expression of the fact that every atom is at zero distance from itself), all the remaining peaks of any magnitude in both sections are of about the same height, and as the superimposed skeleton formulas show, they can be identified as C—S peaks. If these identifications are correct, the structure is thus built up of molecules in which the terminal atoms of the isoprene chain have been linked to sulfur to form a heterocyclic ring, as previously assumed by organic chemists. The fact that all the peaks expected from C—S distances appear in the two sections, and are all of about the same height, shows that the C_4S ring is approximately planar, and parallel to the crystallographic (010) plane. No peaks appear in Figures 1 and 2, which might be associated with S—O distances and indeed if, as would seem probable, the oxygen atoms are attached to the sulfur atom in such a way as to give a tetrahedal distribution of the four sulfur valencies; then a S—O peak should appear at about $y = 1/12$. A section of the F^2-synthesis was made at $y = 1/12$, and a peak of appropriate height was found; its y coördinate was determined more exactly by a line synthesis parallel to the b-axis.

The approximate coördinates deduced from these F^2-syntheses (taking into account the best available data on bond lengths) were used to calculate the structure factors of all planes with a spacing greater than 1.5 A. As the agreement with the experimental values was satisfactory, the latter were given the

phase angles (integral multiples of $\pi/2$) obtained in the calculations, and electron densities were evaluated by means of three-dimensional syntheses over appropriate regions in the unit cell. Successive structure factor calculations and syntheses, introducing all the available terms, were made; the result of the sixth and final synthesis is given in Figure 3, which shows the section at $y = \frac{1}{4}$,

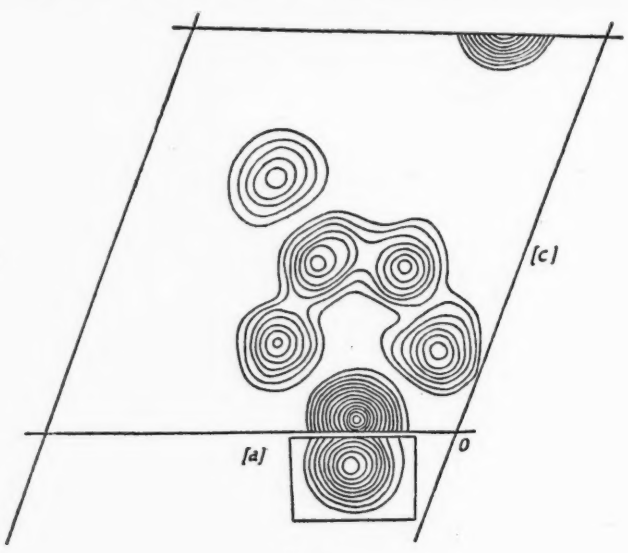


FIG. 3

with the section at $y = 0.095$ inset. The contours are drawn at intervals of one electron/A^3 (the zero contour being omitted), except in the case of the sulfur atom, where the interval between the contours is two electrons/A^3.

The final coördinates are given in Table I.

TABLE I

	x	y	z
S	0.262	0.250	0.031
C_1	0.120	0.250	0.203
C_2	0.276	0.250	0.408
C_3	0.490	0.250	0.424
C_4	0.520	0.250	0.226
C_5	0.678	0.250	0.639
O	0.226	0.095	−0.095

The mean difference between these coördinates and those deduced from the penultimate synthesis is 0.0018, corresponding to about 0.013 A. The experimental structure factors are compared diagrammatically in Figure 5, with the values calculated from the above final coördinates.

The general agreement shown in this diagram is satisfactory, indicating the correctness of the interpretation of the syntheses, and confirming the validity of the assumption that the molecules lie in the planes of symmetry of the space-group $P2_1/m$. A more searching test of this assumption was made as follows: any small displacement of atoms out of the symmetry planes will have the smallest effect on (*hol*) structure factors, and the largest effect on structure

factors of planes with high values of k; accordingly, the differences between $F_{calc.}$ and $F_{obs.}$ were averaged first for thirty (*hol*) planes, and secondly, for an equal number of planes with k greater than 5. In the first case the mean difference was found to be 2.10, and in the second case only 2.00; it is therefore inferred that, within the limits of accuracy of the analysis, the molecules possess planes of symmetry and the space-group is $P2_1/m$.

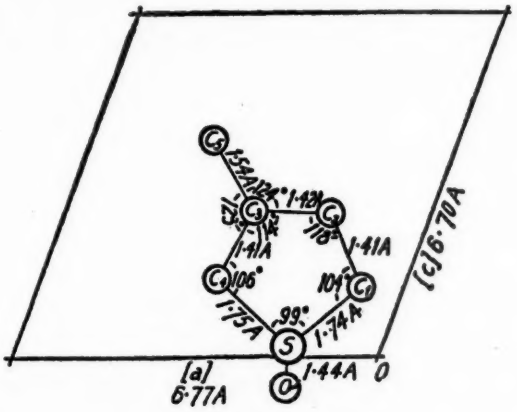


FIG. 4

The interatomic distances and valency angles derived from the final coordinates are given below, and a diagram of the molecule is shown in Figure 4. As a result of the symmetry, the two S—O distances are equal, and the angle O—S—O is bisected by the plane of the carbon atoms.

TABLE II

S—C_1	1.74 A.	C_1—S—C_4	99°
S—C_2	1.75	O—S—O	112 1/2
S—O	1.44	S—C_1—C_2	104 1/2
C_1—C_2	1.41	S—C_4—C_3	105 1/2
C_2—C_3	1.42	C_1—C_2—C_3	117 1/2
C_3—C_4	1.41	C_2—C_3—C_4	113 1/2
C_3—C_5 (methyl)	1.54	C_2—C_3—C_5	123 1/2
		C_4—C_3—C_5	123

The shorter intermolecular distances are:

C_3——O 3.71 A., O——O 3.93 A., O——C_1 3.45 A.
C_5——C_2 3.89 A., C_5——C_3 4.00 A., and C_3——C_3 4.00 A.

Of these, the first is between molecules in the same plane and the others are between molecules in planes 1/2*b* apart.

The interatomic distances given above are considered to be accurate to about 0.02 A., and the angles to 2°. The sulfur-oxygen distance is in good agreement with other recent x-ray and electron diffraction values, *e.g.*, 1.44 ± 0.03 A. in potassium sulfamate[3], 1.45 ± 0.02 A. in thionyl chloride, and 1.43 ± 0.02 A. in sulfuryl chloride[4], and the sulfur valency angles are roughly tetrahedal, as would be expected. The S—C bonds are shorter than the sum of the usually accepted single bond radii (1.81 A.) and, although the C_3—C_5 (methyl) bond is exactly that to be expected for a single bond, the other

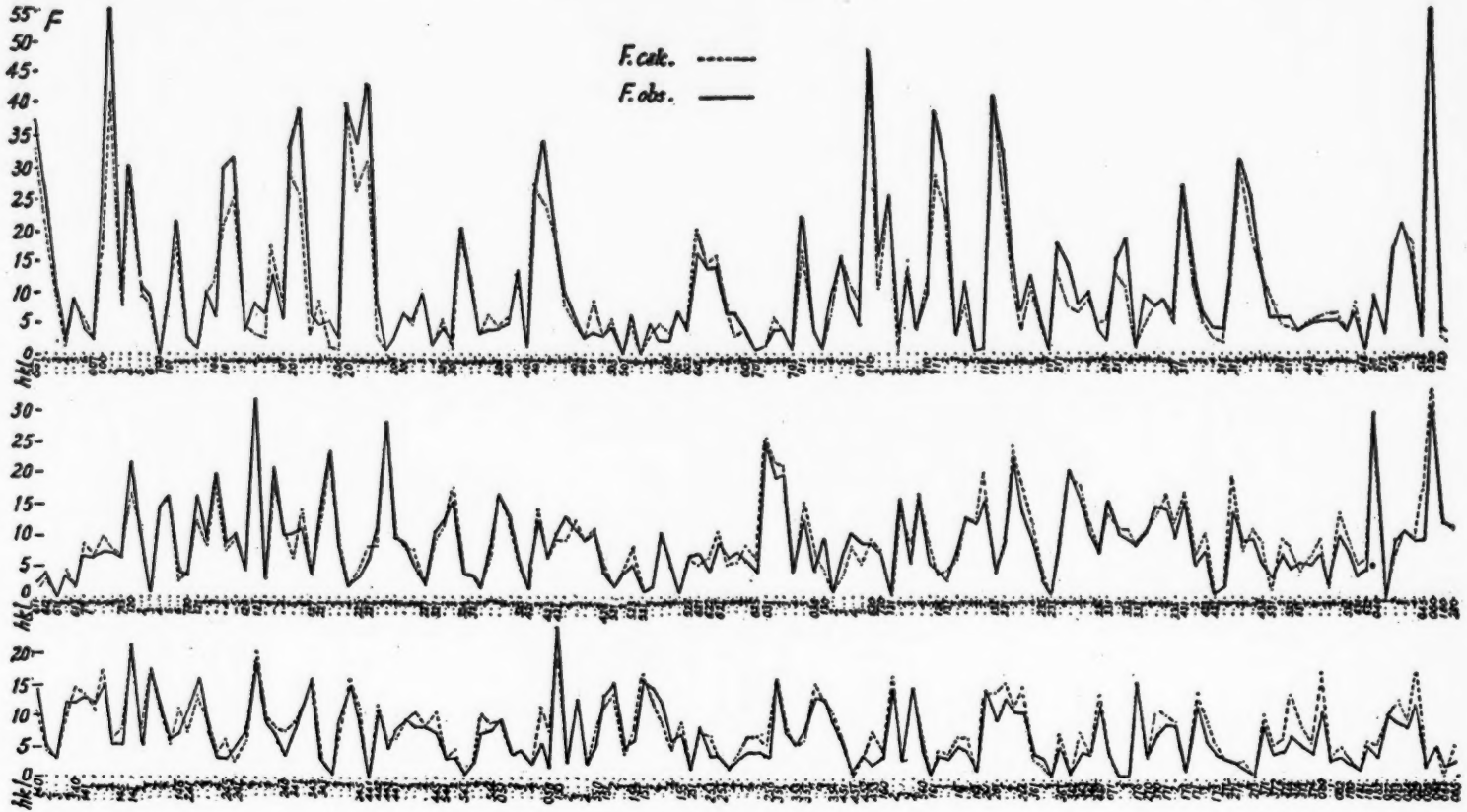
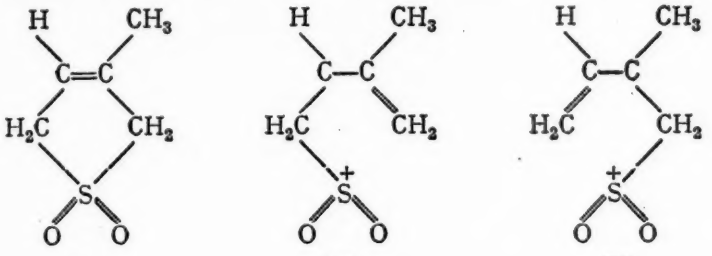


FIG. 5

carbon-carbon distances are considerably shorter; thus while the bonds external to the heterocyclic ring are normal, all those in the ring are intermediate in length between single and double bonds.

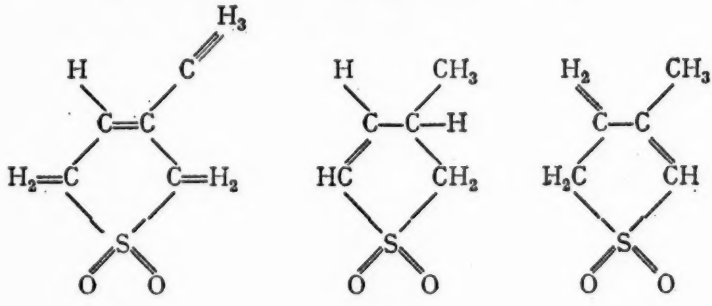
Although the evidence could not be regarded as entirely satisfactory, β-isoprene sulfone has been ascribed the structure I on chemical grounds[5].



I. II. III.

If the bond lengths reported above are accepted, it is clear that I does not adequately represent the structure, since it would require two single carbon-carbon bonds of length about 1.54 A., and one double bond of about 1.34 A. in the ring; the notable feature of the experimental results is that these three bonds are equal within the errors of measurement, and of length intermediate between single and double bonds. We suggest, therefore, that β-isoprene sulfone has a structure involving resonance between I and the ionized forms II and III in approximately equal measure; equal contributions from these three forms would be expected to give three equal C—C bonds of about 1.43 A. in length, each possessing about 33 per cent double bond character. The formulation of the sulfone as a resonance structure involves a type of valency binding which is rather uncommon among organic compounds, but which is similar to that supposed to exist in other sulfur compounds[6].

The structure now suggested implies that the C—S bonds will be approximately two-thirds single bond and one-third semi-ionic in character, and it is difficult to predict what effect this will have on the interatomic distance; the observed value is about 0.06 A. less than the predicted single-bond distance.



IV. V. VI.

If I is written in the form IV it will be observed that there is the possibility of "hyperconjugation"[7], and it is conceivable that this may account in some measure for the observed results, although the normal value of 1.54 A. obtained for the C—C (methyl) bond length is against this.

It was shown by Eigenberger[8] that, when the normal or β-form of isoprene sulfone is treated with aqueous or alcoholic potassium hydroxide in ultraviolet light, it is converted into an equilibrium mixture containing about 8 per cent of the original substance and 92 per cent of a new compound of identical analysis and molecular weight, but different chemical and physical properties.

Boeseken and van Zuydewijn[5] and Backer, Strating and Zuithoff[5] have suggested that this new substance, which is called α-isoprene sulfone, is an isomer with the structure V or VI.

A preliminary x-ray examination of this substance was made, and its monomeric character was confirmed, but a detailed analysis was not considered to be justified at the present time. It is of interest to note that if the hydrogen atoms in α-isoprene sulfone are attached to the carbon atoms, as indicated in V or VI, it is impossible to formulate ionized structures similar to II and III without transgressing the octet rule for at least one carbon atom, and a resonance structure is not to be expected. Hyperconjugation effects, on the other hand, would be expected to be quite as marked in VI as in IV. It is hoped to investigate the α-form in more detail later.

In view of the somewhat unexpected nature of the structure of β-isoprene sulfone, it is uncertain how far the results are directly applicable to isoprene units in "crystalline" rubber. Its structure, however, may well have some bearing on certain rubber problems, and it is interesting to note that structures involving comparable C_4S rings have been proposed for ebonite[9].

The above work has been carried out as part of the program of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

To meet the need for economy in the use of paper, full numerical tables of observed and calculated values have been omitted. The experimental portion of the paper has also been omitted, but the original draft may be inspected by any member of the Society who is interested, on application to the Secretary.

SUMMARY

A detailed x-ray analysis has shown that the molecule of β-isoprene sulfone has a heterocyclic structure, in which resonance occurs between the three carbon-carbon bonds of the C_4S ring. The bond lengths are C—C (in the ring) 1.41 A., C (ring)—C (methyl) 1.54 A., C—S 1.75 A., and S—O 1.44 A., all $\pm$ 0.02 A.; the distribution of the four sulfur bonds is approximately tetrahedal.

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MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES OF POLYISOBUTYLENES *

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INTRODUCTION

The extensive investigations carried on by Staudinger and his coworkers during the past thirteen years have done much to stimulate interest in one of the most important phases of high polymer chemistry, namely, the assignment of molecular weight values to these substances. Early in the course of these investigations, and on the basis of extremely meager experimental evidence, Staudinger[1] proposed his well-known relationship of proportionality between the molecular weight of a linear polymer and the ratio of the viscosity increment ($\eta_r - 1$) to concentration. With appropriate revisions introduced by Kraemer and Lansing[2], this may be written:

$$[\eta] = K_S \bar{M}_w \tag{1}$$

where $\bar{M}_w$ is the weight average molecular weight, K_S is a constant and $[\eta]$ is the intrinsic viscosity[3], or limiting ratio of viscosity increment to concentration, defined by:

$$[\eta] = [(\eta_r - 1)/c]_{c=0} \equiv [(\ln \eta_r)/c]_{c=0} \tag{2}$$

η_r is the relative viscosity and c is the concentration in g. of solute per 100 cc. of solution. Staudinger and his coworkers proceeded to determine the constant K from the intrinsic viscosities of low polymers in the molecular weight range of a few thousand or less where cryoscopic or ebullioscopic methods are applicable. By extrapolating Equation (1) far beyond the range for which K was determined, they arrived at molecular weights of the order of a hundred thousand for cellulose derivatives, vinyl resins, polystyrenes and rubber. Since viscosities are easily measured, Equation (1) appeared to offer a most attractive method for determining average molecular weights.

More recent work, much of it by Staudinger and his collaborators[4], has shown that these values are too low; the constant K appears to decrease as the molecular weight increases. In each proved case of disagreement with his "rule" (the exceptions to which now far outnumber the instances of agreement) Staudinger insists that this is due to some peculiarity of the particular type of polymer molecule, *e.g.*, to an exceptional chain configuration or to branched chain structure[5]. Meyer[6], who has persistently attacked the quantitative validity of Staudinger's equation, concludes that divergence from (1) cannot be regarded as an indication of branched, or nonlinear, polymer structure, since there is no assurance that a given linear polymer will obey Equation (1)[7].

Viscosity measurements on solutions of polyoxyethylene glycols[8] in the molecular weight range of 1000 to 8200, and on polyesters[9] up to molecular weights of 30,000 (weight average) support a modified form of (1) in which a constant term has been added. Although available data pertaining to poly-

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mers of higher molecular weights indicate that Staudinger's equation is generally inapplicable, they are inadequate for conclusively establishing accurate relationships between molecular weight and intrinsic viscosity. For this purpose it is necessary to obtain intrinsic viscosities and absolute molecular weight values for a series of samples of a given polymer series having molecular weights distributed over a wide range. Inasmuch as the viscosity generally depends on a different type of average molecular weight from that obtained by the absolute method employed (*cf. seq.*), the samples must be rendered as homogeneous as possible with respect to molecular weight (unless the type of distribution within each sample is known).

In the present investigation, intrinsic viscosities of carefully fractionated polyisobutylenes have been compared with their absolute number average molecular weights determined by an osmotic pressure method. The higher polyisobutylenes (above approximately 400,000) possess molecular weights more than ten times the values obtained by extrapolating Staudinger's Equation (1)[10]. The existence of a simple empirical relationship between intrinsic viscosity and molecular weight has been established.

EXPERIMENTAL

Polymers.—Relevant data concerning the polymers from which the fractions were prepared are given in Table I. They were prepared by conventional

TABLE I

Polymer	Temperature of preparation (° C)	Catalyst	$[\eta]^a$
A	−27	$AlCl_3$	0.33
B	−85	BF_3	1.99
C	−78	$AlCl_3$	1.35
D	−47	BF_3	0.29

[a] Intrinsic viscosity measured in diisobutylene at 20°.

low temperature polymerization techniques[11], using the catalysts indicated. In the preparation of polymer D, *n*-butylenes were intentionally mixed with the isobutylene to obtain a product of low average molecular weight. The *n*-butylenes act as poisons, without entering the polymer to an appreciable degree[11].

Fractionation.—A fractional precipitation procedure essentially similar to those previously applied to cellulose[12] and cellulose derivatives[13] and to various resins[14] was employed. Pure benzene (Barrett, "thiophene-free" grade) was used as the solvent, and C.P. acetone, dried and redistilled, was used as precipitant. From 15 to 25 g. of polyisobutylene was dissolved in from two to three liters of benzene. A quantity of acetone slightly in excess of that required for incipient cloudiness at 25.0° was added. The solution was rendered homogeneous by warming, and allowed to cool slowly with gentle stirring for about two hours, after which it was immersed in a water thermostat maintained at 25.00 ± 0.05°, the stirring being continued for an additional thirty minutes. The stirrer was removed, and the gelatinous precipitate was allowed to agglomerate and settle on the bottom of the flask for at least two hours, or until the supernatant solution became clear. The liquor was carefully decanted, with due exercise of caution to prevent decantation of any of the precipitate. The precipitate was redissolved in a liter of warm benzene, and sufficient acetone was added to reproduce the same concentration (cc. of acetone per 100 cc. of benzene) used in the first precipitation. After reprecipi-

tating and pouring off the liquor exactly as described above, the precipitate was steeped in methanol and dried at 70° in vacuum for two hours. The low molecular-weight, highly plastic fractions were redissolved in benzene, recovered in a suitable container by evaporation on the steam-bath, then dried as above. Repetition of vacuum drying several days later brought the samples effectively to constant weight. This procedure proved preferable to a single prolonged drying period at 70°.

The combined liquors from the above precipitations were evaporated to a small volume at about 60° in a stream of air in order to remove the acetone completely. Benzene was added to bring the solution to a volume of two liters, and acetone was added to a concentration slightly greater than that used in the preceding precipitation. The precipitation and reprecipitation of the second fraction were carried out as described above. Proceeding in this way, there was obtained a series of fractions of regularly decreasing molecular weight, each fraction being the product of two precipitations. As the quantity of unprecipitated polymer decreased, the volume of the solution from which precipitation occurred was decreased accordingly. For the first precipitation of each fraction polymer, concentrations were maintained in the vicinity of 1 g. per 100 cc. of solution and, for the reprecipitation, from 0.1 to 0.2 g. per 100 cc. The desirability of using dilute solutions to obtain good fractionation has been pointed out by Schulz[15]. Consideration of the equilibria between the highly swollen precipitated phase and the "solvent" phase leads to similar conclusions[16].

The sum of the products of the weight fraction times the intrinsic viscosity for each fraction was equal to the intrinsic viscosity of the original polymer, within experimental error. Thus, degradation did not occur during the fractionations.

Intrinsic viscosities.—Viscosities were measured in diisobutylene solution at 20.0°, using carefully calibrated Ubbelohde suspended level viscometers. Empirical kinetic energy corrections were employed. Since the times of flow were of the order of 100 sec., these were invariably small. Suspended foreign matter was removed by filtration immediately preceding measurement.

Concentrations were suitably chosen to obtain relative viscosities in the range 1.15 to 1.4. Values of $(\ln \eta_r)/c$ calculated from relative viscosities in this range differed by less than 2 per cent from the infinite dilution values[17]. Hence, they were accepted as intrinsic viscosities (see Equation (2)) without extrapolation. Generally two values of $[\eta]$ agreeing within 2 per cent were obtained.

Osmotic pressure determination.—The osmometers[18] which have been used are similar in design to one described by Meyer, Wolff and Boissonnas[19]. Each of them consists of two brass blocks, 4″ × 4″ × ½″, into the faces of which shallow cylindrical cells have been cut. The blocks are bolted firmly together with the membrane separating the cells. The membrane also acts as a gasket to prevent leakage between the blocks. In use the osmometer is placed with the faces of the block vertical. The cell containing pure solvent communicates with an upright Pyrex capillary of approximately 0.5 mm. bore; connection is provided by a metal-to-glass seal to a "Kovar" alloy[20] tube ⅛″ in diameter, which in turn is soldered into a small hole leading to the top of the solvent cell through the upper edge of the brass block. The solution cell connects similarly to a larger upright tube in which another capillary tube of the same bore can be inserted. The difference in hydrostatic head between the two cells can be varied by raising or lowering this tube. An additional connection with each

cell, by means of a small hole drilled downward from the upper edge of the block and meeting a horizontal hole drilled from the bottom edge of the cell, permits changing solution or solvent without dismantling the osmometer. A needle valve at the top of the hole effectively seals this connection during use.

The cells of the first osmometer to be constructed consist simply of shallow cylindrical holes 2¼″ in diameter by $\frac{3}{16}$″ in depth. The membrane is supported on either side by brass disks $\frac{1}{16}$″ thick, drilled with numerous ¼″ holes. The disk for the solvent compartment was covered with a fine metal screen on the face next to the membrane. The disks fit into indentations around the rim of the cell. These indentations were carefully machined to assure light contact between the disks and the membrane without preventing the outer portions of the membrane from sealing the osmometer.

The cells of the second osmometer were cut into the blocks by machining within a 2¼″ circular area diagonal grooves ⅛″ wide by ⅛″ deep with semicircular profile at their base[21]. Two sets of parallel grooves, each set perpendicular to the other, were cut across the area. The grooves were spaced $\frac{3}{16}$″ apart, center to center, leaving island points $\frac{1}{16}$″ square for supporting the membrane. To eliminate "dead end" channels, a circular groove was cut around the periphery of the cell area. The sets of points on the two blocks coincided accurately. One set of supporting points was machined down 0.002″ below the level of the surface of the surrounding block to assure sufficient pressure on the portion of the membrane surrounding the cell to tightly seal the osmometer. With this arrangement, over 95 per cent of the membrane covering the cell area is in contact with solvent and solution, compared with 50 per cent for the other osmometer. Furthermore, there are no inaccessible crevices which would retain solution when the cell is emptied and hinder rapid attainment of equilibrium when filled. The cells of each osmometer hold about 8 cc. of liquid.

Two types of membranes were used. The first consisted of swollen cellophane[22], No. 600, without waterproofing. After soaking the membrane in hot distilled water for a few minutes, it was placed in 7 *N* aqueous ammonium hydroxide for one hour at room temperature. It was then washed successively in distilled water, in alcohol, in a mixture of equal parts of alcohol and the solvent to be used, and finally in the pure solvent.

Much more permeable membranes were made by denitrating collodion films, according to the procedure described by Montonna and Jilk[23]. About 40 cc. of a mixture of 3 parts of Merck C.P. collodion (5 per cent) and one part of ether was placed within an iron ring 5″ in diameter floating on a quiescent surface of clean mercury. The solvent was allowed to evaporate slowly until the membrane became sufficiently rigid to be removed from the ring. The last traces of solvent were removed by soaking in water. The outer edge of the membrane of irregular thickness was cut away. Denitration was carried out with ammonium hydrosulfide, exactly as described by Montonna and Jilk[23]. The denitrated membrane was washed thoroughly with water (instead of carbon disulfide[23]). Transfer to the organic solvent was carried out as described above for the cellophane membranes.

The more permeable denitrated collodion membranes could not be used for polymer fractions below about 50,000 average molecular weight because of passage of some of the polymer components through the membrane. When one of these membranes was used for a fraction below this limit, the observed pressure difference drifted downward and the liquid removed from the solvent compartment was found to contain a small amount of polymer. With higher

fractions, the liquid removed from the solvent compartment was free of non-volatile material. The cellophane membranes, on the other hand, gave no evidence of solute permeation down to a molecular weight of about 5000 (see Table III). Consequently, cellophane membranes were used for low molecular-weight fractions. Solutions of fractions above 50,000 average molecular weight yielded the same osmotic pressures with either type of membrane.

The osmometers were assembled as follows. The solvent cell, placed in a horizontal position, was filled with solvent. The membrane was set in place and the block containing the solution cell was set in place immediately without allowing the membrane to dry. The blocks were firmly bolted together. The solution cell was filled through the needle valve opening[19] leading to the bottom of the cell, then emptied by applying pressure to the upper opening, and refilled with fresh solution. Bubbles in either compartment were readily removed by oscillating the levels gently, after which the needle valves were inserted and tightened. Liquid levels were adjusted by adding (or removing) solution and solvent through the upper ends of the upright glass tubes connecting with the cells. At the end of an experiment the needle valve was removed from the solution compartment, and the solution was blown out. The cell was filled twice with the next solution to be measured and emptied, and refilled a third time to ensure adequate rinsing. In this way the same membrane could be used over and over again. When it was desirable to do so, the solvent could be similarly replaced.

To eliminate fluctuations in the solvent level due to temperature variations, the cell was immersed in a water thermostat held at 25.00°, in which temperature fluctuations amounted approximately to ±0.001°. Levels in the capillaries were read to 0.005 cm., with a cathetometer. The capillary inserted in the large tube connecting with the solution cell and the capillary attached to the solvent cell were cut from the same piece of tubing of calibrated uniform bore. The mean diameter varied by no more than ±0.5 per cent. Since the capillary rise was of the order of 2 cm., the error due to difference in capillary rise in the two tubes was only about ±0.01 cm.

After placing the osmometer in the bath and adjusting the difference in levels to approximate the expected osmotic pressure, the position of the levels was measured with the cathetometer from time to time. After an hour or two, the levels were readjusted toward the approximate equilibrium value predicted empirically from the trend of the difference in levels. In some instances a second adjustment was made after another interval. Measurements were continued until the difference in level became constant within ±0.01 cm. change per hour. As the difference in densities of solvent and solution were negligible for the dilute solutions under investigation, the osmotic pressure in g. per sq. cm. was taken equal to the product of the solvent density and the difference in level in cm. This essentially static method proved to be more reliable and accurate than a more rapid dynamic method.

The course of the approach to equilibrium is shown in Figure 1. After equilibrium has been attained, displacement of the level in either direction is followed by gradual return to the same equilibrium pressure. There was no significant drift in the equilibrium pressure up to at least three days. The rate of approach to equilibrium was about 2 to 5 per cent per minute for the denitrated collodion membranes; for the cellophane membranes the rate was about one-tenth of this, the values in each case varying somewhat from membrane to membrane. The apparent rate depends not only on the specific permeability of the membrane, but also on the rigidity with which the mem-

brane is held in place. The advantage of greater specific permeability gained by the use of thinner membranes is outweighed by the decrease in rigidity. With the denitrated collodion membranes, equilibrium could usually be reached within about four or five hours; at least eight hours was required for the cellophane membranes.

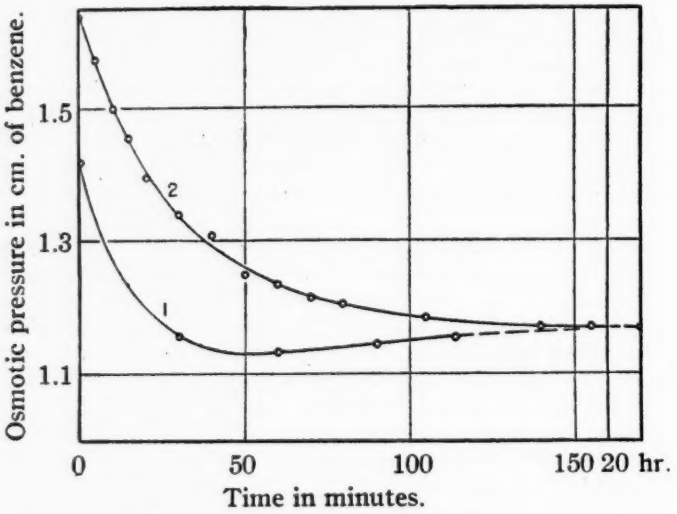


FIG. 1.—Establishment of osmotic equilibrium. After completing the observations shown on curve 1, the pressure was intentionally increased above the equilibrium value; the subsequent decrease in pressure is shown by curve 2 (Polymer C (4–9), 1.00 g./100 cc. in benzene; denitrated collodion membrane).

Occasionally the solution compartment was filled with solvent, and any equilibrium difference in level (apparently due to leakage) was observed. Generally this difference was less than ± 0.02 cm., and for the more accurate work it was required to be so (*e.g.*, in experiments pertaining to osmotic pressure-concentration relationships)[24]. In determinations on low molecular weight samples, where the resulting error was not significant, somewhat larger "residual" values were tolerated with the introduction of corresponding corrections on the observed osmotic pressures for the solutions. With solutions of high viscosity (higher concentration and molecular weight), the ultimate attainment of true equilibrium was slower[24], although the permeability of the membrane naturally was the same. The difference is believed to arise from slow equilibration within the solution itself[25].

RESULTS

Osmotic pressure-concentration relationships.—For correct evaluation of the number average molecular weight, it is absolutely essential to extrapolate the osmotic pressure-concentration ratio π/c to zero concentration. This is especially important when dealing with high polymer solutions because of their rapid deviations from ideal solution laws at finite concentrations[26].

For the purpose of establishing reliable procedures for extrapolation to zero concentration, osmotic pressures of several fractions differing in molecular weight were measured at 25.0° in cyclohexane and in benzene at various con-

centrations up to 2 g. per 100 cc. Attainment of the utmost accuracy was emphasized particularly in this portion of the investigation. The results are given in Table II. The polymer fractions are designated in the first column by a letter referring to the polymer from which the fraction was prepared (see Table I), followed by two numbers in parentheses which refer to the amounts of precipitant used in the isolation of the sample. Thus, C (4–9)

TABLE II

OSMOTIC PRESSURE *vs.* CONCENTRATION IN CYCLOHEXANE AND BENZENE AT 25.0°

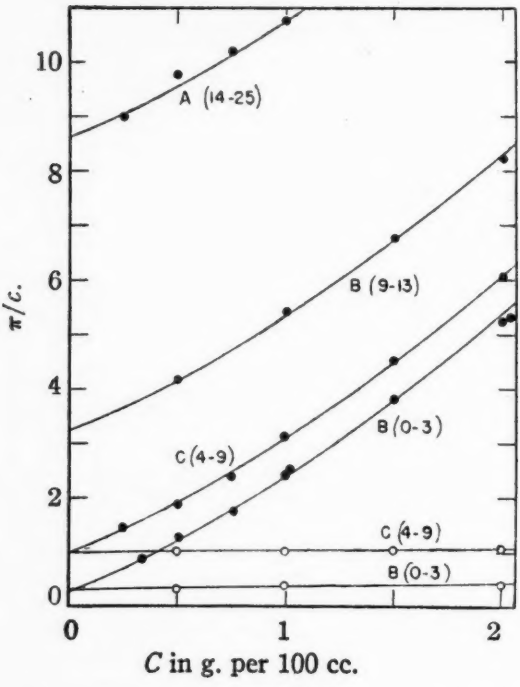
Polymer and solvent		c in g./100 cc.	π in g./sq. cm.	π/c	$\pi/c - (\pi/c)_0$
B (0–3)	C_6H_{12}	2.04	10.82	5.31	5.01
B (0–3)	C_6H_{12}	2.00	10.58	5.29	4.99
B (0–3)	C_6H_{12}	1.50	5.73	3.82	3.52
B (0–3)	C_6H_{12}	1.02	2.57	2.52	2.22
B (0–3)	C_6H_{12}	1.00	2.42	2.42	2.12
B (0–3)	C_6H_{12}	0.76	1.32	1.74	1.44
B (0–3)	C_6H_{12}	.51	0.65	1.27	0.97
B (0–3)	C_6H_{12}	.34	.30	0.88	.58
		.00		(.30)[a]	
B (0–3)	C_6H_6	2.00	.82	.41	.08
B (0–3)	C_6H_6	1.00	.37$_5$	.37$_5$	.04$_5$
B (0–3)	C_6H_6	1.00	.40^5	.40^5	.07^5
B (0–3)	C_6H_6	0.50	.15$^5_5$	.31^5	−.02^5
B (0–3)	C_6H_6	.50	.17$^5_5$	.35	.02
		.00		(.33)	
C (4–9)	C_6H_{12}	2.00	.12.10	6.05	5.06
C (4–9)	C_6H_{12}	1.50	6.80	4.53	3.54
C (4–9)	C_6H_{12}	1.00	3.12	3.12	2.13
C (4–9)	C_6H_{12}	0.75	1.79	2.39	1.40
C (4–9)	C_6H_{12}	.50	0.93$_5$	1.87	0.88
C (4–9)	C_6H_{12}	.25	.36^5	1.44	.45
		.00		(0.99)	
C (4–9)	C_6H_6	2.00	2.14$_5$	1.07	.08
C (4–9)	C_6H_6	1.50	1.57$^5_5$	1.05	.06
C (4–9)	C_6H_6	1.00	1.02$^5_5$	1.02$_5$	.03$_5$
C (4–9)	C_6H_6	0.50	0.50$^5_5$	1.01^5	.02^5
		.00		(0.99)	
B (9–13)	C_6H_{12}	2.00	16.41	8.20	4.96
B (9–13)	C_6H_{12}	1.50	10.12	6.75	3.51
B (9–13)	C_6H_{12}	1.00	5.39	5.39	2.15
B (9–13)	C_6H_{12}	0.50	2.07$_5$	4.15	0.91
		.00		(3.24)	
A (14–25)	C_6H_{12}[b]	1.00	10.77	10.77	2.10
A (14–25)	C_6H_{12}[b]	0.75	7.64	10.19	1.52
A (14–25)	C_6H_{12}[b]	.50	4.89	9.78	1.11
A (14–25)	C_6H_{12}[b]	.25	2.25	9.00	0.33
		.00		(8.67)	

[a] The π/c values in parentheses have been obtained by extrapolation.
[b] A cellophane membrane was used in the experiments on A (14–25). Denitrated collodion membranes were used in all other experiments.

refers to a fraction prepared from polymer C, which remained in the liquors from the standard precipitations (see above) using 4 cc. of acetone per 100 cc. of benzene, but which was precipitated by 9 cc. of acetone per 100 cc. of benzene. It has been found that the region of precipitation for a given concentration of acetone is accurately reproduced with different polymers, despite wide variations in their distributions and average molecular weights[27]. Thus, the figures in parentheses are indicative of the molecular weight region covered by the fraction. To obtain fractions of sufficient size for this work, it was

expedient to separate comparatively broad cuts, which consequently are not as homogeneous as the fractions used in the investigation of the intrinsic viscosity-molecular weight relationship.

The ratios of π/c given in the fourth column of Table II are plotted against c in Figure 2. A linear relationship between π/c and c has been deduced on theoretical grounds by Huggins[28] and the author[16] and, in general, experimental investigations[29] on various polymer solutions seem to support this deduction. The points for the cyclohexane solutions definitely describe curves with upward



C in g. per 100 cc.

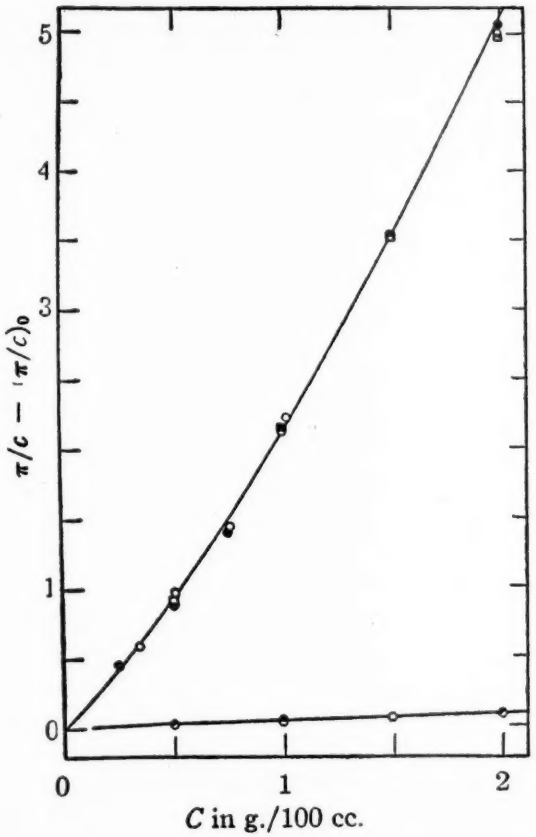
FIG. 2.—Osmotic pressure-concentration ratio *vs.* concentration for cyclohexane (●) and benzene (○) solutions.

concavity. A similar curvature in the plot of π/c *vs.* c for rubber solutions in benzene has been observed by Gee and Treloar[24]. They contend furthermore that the slope at a given concentration varies with the molecular weight of the sample. Over the range investigated here, no definite dependence of slope on molecular weight has been observed for polyisobutylene solutions. To demonstrate this, the curves in Figure 2 for the cyclohexane solutions have been drawn purposely with identical shapes, so that they are all superimposable by suitably shifting the ordinate axes. This is further shown by the $(\pi/c) - (\pi/c)_0$ values given in the last column of Table II and plotted against c in Figure 3. This quantity, which may be looked upon as the deviation from the classical ideal solution law, varies with concentration in a manner which shows no significant dependence on molecular weight.

The π/c values for benzene solutions of polyisobutylene exhibit much smaller variations with concentration (see Figure 2 and the last column of

Table II), as would be expected[16] from the fact that polyisobutylene of high molecular weight is on the verge of precipitation when dissolved in benzene at 25°[30]. Straight lines with small positive slope have been drawn through these points. Values of $(\pi/c) - (\pi/c)_0$ for benzene solutions are also plotted in Figure 3.

The significant feature of the results shown in Figure 2, so far as the present investigation is concerned, is the gratifying coincidence of the extrapolations



C in g./100 cc.

FIG. 3.—Deviation from van't Hoff's law *vs.* concentration for cyclohexane (upper curve) and benzene (lower straight line) solutions: ● = B (0–3); ○ = C (4–9); □ = B (9–13).

of the curves for the same polymer in cyclohexane and in benzene, in spite of the marked difference in the dependence of π/c on concentration. This fact confirms the reliability of the extrapolation procedure for the purpose of determining $(\pi/c)_0$, and, hence, the number average molecular weight. Most of the molecular weight determinations have been carried out in cyclohexane; for the samples of highest molecular weight benzene has been used. Extrapolations to infinite dilution have been based on the curve and straight line in Figure 3 representing $\pi/c - (\pi/c)_0$ *vs.* c for cyclohexane and benzene solutions, respectively.

Molecular weight-intrinsic viscosity relationship.—The van't Hoff equation:

$$\bar{M}_n = RT/(\pi/c)_0$$

relating number average molecular weight to π/c *at zero concentration* possesses an indisputably rigorous thermodynamic basis. With the osmotic pressure in g. per sq. cm., c in g. per 100 cc. and $T = 298°K$ this becomes:

$$\bar{M}_n = 2.53 \times 10^5/(\pi/c)_0$$

Intrinsic viscosities in diisobutylene and osmotic pressure results leading to values of $\bar{M}_n$ computed from this equation are presented in Table III for

TABLE III

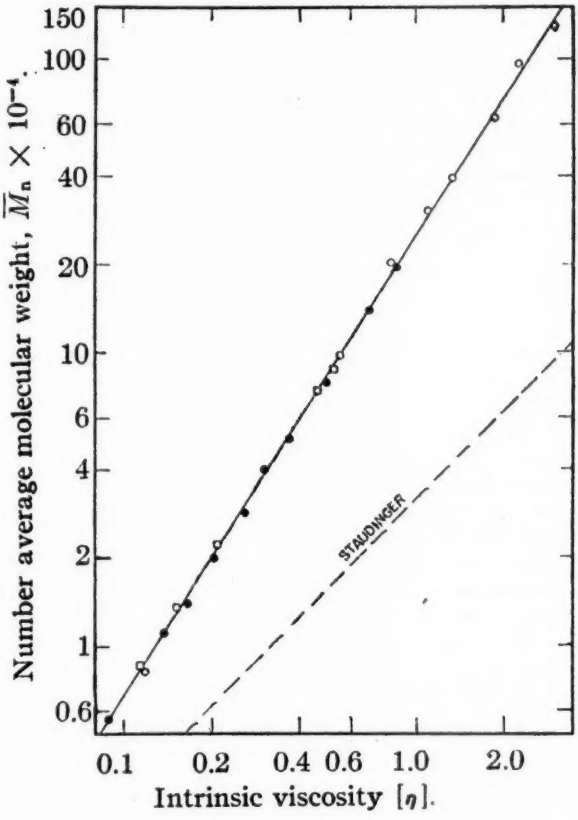
MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES[a] OF POLYISOBUTYLENE FRACTIONS

Polymer	$[\eta]$	Membrane[b] and solvent		c, g./100 cc.	π, g./sq. cm.	π/c	$(\pi/c)_0$	$\bar{M}_n$
A (7–8)	0.866	Col.	C_6H_{12}	0.50	1.08	2.16	1.25	202,000
				1.00	3.44	3.44	1.34	189,000
A (8–9)	.698	Col.	C_6H_{12}	0.50	1.38$_5$	2.77	1.86	136,000
				1.00	3.89^5	3.89	1.79	141,000
A (10–12)	.495	Col.	C_6H_{12}	0.50	2.05	4.10	3.19	79,300
				1.00	5.32	5.32	3.22	78,600
A (12–14)	.370	Col.	C_6H_{12}	0.50	2.94	5.88	4.97	50,900
				1.00	7.06	7.06	4.96	51,000
A (14–17)	.303	Col.	C_6H_{12}	0.51	3.73	7.31	6.38	39,700
A (17–20)	.260	Col.	C_6H_{12}	.47	4.61	9.80	8.94	28,300
A (24–30)	.203	Col.	C_6H_{12}	.37$_5$	5.04	13.43	12.77	19,800
A (30–40)	.165	Col.	C_6H_{12}	.37$_5$	7.04	18.77	18.11	13,970
				.75^5	14.80	19.75	18.28	13,830
A (40–55)	.137	Col.	C_6H_{12}	.50	11.97	23.94	23.03	10,980
				.25	5.78	23.12	22.70	11,130
A (55–85)	.118	Cel.	C_6H_{12}	.25	7.85	31.40	30.98	8,170
A (85–125)	.089	Cel.	C_6H_{12}	.25	11.36	45.44	45.02	5,620
				.37$_5$	17.0	45.4	44.8	5,660
B (2.5–3)	3.04	Col.	C_6H_6	1.00^5	0.23$_5$	0.23$_5$	0.19$_5$	1,300,000
				1.00	.23^5	.23^5	.19^5	1,330,000
C (3–3.5)	2.29	Col.	C_6H_6	1.00	.30	.30	.26	970,000
				0.50	.14	.28	.26	970,000
C (3.5–4)	1.87	Col.	C_6H_6	1.00	.44$_5$	.44$_5$	.40$_5$	625,000
				0.50	.21$_8$	.43^5	.41^5	608,000
C (4.5–5.5)	1.35	Col.	C_6H_{12}	0.50	.76^5	1.53^5	.62^5	408,000
				1.00	2.77^5	2.77	.67	378,000
C (5.5–6.5)	1.12	Col.	C_6H_{12}	0.50	0.87	1.74	.83	304,000
				1.00	2.92	2.92	.82	308,000
C (6.5–8)	0.83	Col.	C_6H_{12}	0.50	1.11	2.22	1.31	193,000
				1.00	3.29	3.29	1.19	213,000
		Cel.	C_6H_{12}	1.00	3.33	3.33	1.23	206,000
C (10–12)	.551	Col.	C_6H_{12}	0.50	1.74	3.48	2.57	98,400
				0.50	1.73	3.46	2.55	99,200
				1.00	4.66	4.66	2.56	98,800
D (10–11)	.522	Col.	C_6H_{12}	0.50	1.90	3.80	2.89	87,500
				1.00	4.99	4.99	2.89	87,500
D (11–12)	.460	Col.	C_6H_{12}	0.50	2.18	4.36	3.45	73,300
				1.00	5.64	5.64	3.54	71,500
D (25–29)	.209	Cel.	C_6H_{12}	0.50	5.98	11.96	11.05	22,900
D (35–43)	.152	Cel.	C_6H_{12}	.25	4.72	18.88	18.46	13,700
				.50	9.91	19.82	18.91	13,370
D (55–67)	.113	Cel.	C_6H_{12}	.25	7.40	29.60	29.18	8,660
				.50	15.25	30.50	29.60	8,540

[a] Intrinsic viscosities measured in diisobutylene at 20.0° collodion and cellophane membranes, respectively.

[b] The abbreviations "Col." and "Cel." refer to denitrated

several series of polyisobutylene fractions, each representing a relatively narrow range of molecular weight. A log-log plot of mean values of $\bar{M}_n$ *vs.* $[\eta]$ is shown in Figure 4 to be strictly linear within experimental error. A broken line of slope equal to unity, representing the Staudinger relationship by means



Intrinsic viscosity $[\eta]$.

FIG. 4.—Log $\bar{M}_n$ *vs.* log $[\eta]$ for polyisobutylene fractions from Polymer A (●), Polymer C (○), Polymer D (□), and from Polymer B (◇). Molecular weights calculated from Staudinger's relationship are shown by the broken line.

of which previous molecular weight values for polyisobutylene have been calculated, is also included.

The equation of the straight line drawn through the points in Figure 4 is:

$$\log M = 5.378 + 1.56 \log [\eta] \tag{4}$$

or

$$[\eta] = KM^a \tag{5}$$

where $K = 3.60 \times 10^{-4}$ and $a = 0.64$. Equation (5) is the equivalent of one recently proposed by Houwink[31] for polymeric methyl acrylate, methyl methacrylate, polyvinyl acetate and polyvinyl alcohol on the basis of results of Staudinger and Warth[5]. These results covered a comparatively brief molecu-

lar weight range, and the effectiveness of the coarse fractionation employed by Staudinger and Warth is suppressing the difference between the "viscosity average" and the number average molecular weights is doubtful. Nevertheless, Houwink[36] found $a = 0.6$, in close agreement with our value for polyisobutylene.

DISCUSSION

Previous comparisons[32] of polyisobutylene solution viscosities with their molecular weights have been confined to the molecular weight range below about 10,000. The single measurement[10] on which Staudinger[33] apparently based his "constant" for polyisobutylene was carried out on a polymer having a cryoscopic molecular weight of 1490 and an intrinsic viscosity in tetralin of 0.044. The molecular weight calculated by extrapolating Equation (4) down to this intrinsic viscosity (ignoring the difference in solvents) is 1800. The discrepancy is no larger than should be expected to arise from the probable degree of heterogeneity of the sample used by Staudinger and Brunner[10].

Kemp and Peters[34] have compared intrinsic viscosities of polyisobutylenes with "molecular weights" calculated from cryoscopic measurements ($\Delta T/c$) at arbitrarily chosen finite concentrations. They reject extrapolated $(\Delta T/c)_0$ values for this purpose on the grounds that they give "inordinately high molecular weights". There is no basis whatever for using anything that can be derived from their results other than $(\Delta T/c)_0$ values, necessarily determined by extrapolation, for the calculation of the number average molecular weight.

Even after extrapolating the results of Kemp and Peters to zero concentration, they are of doubtful value for establishing viscosity-molecular weight relationships because of the ineffective fractionation procedure which was employed in the preparation of their samples. Synthetic polyisobutylenes invariably contain species covering a broad molecular weight range. Kemp and Peters obtained only a few fractions (one of them constituted 88 per cent of the initial polymer) from each synthetic product, and these did not differ greatly in average molecular weight. The conclusion is unavoidable that these fractions consisted of very broad cuts. The viscosity averages of some of their samples may have been several times their number average molecular weights.

There is no actual disagreement between earlier cryoscopic measurements and the osmotic pressure results reported here. The wide discrepancies between previous molecular weight values for polyisobutylenes and those established here result from several factors: (1) failure to extrapolate cryoscopic measurements to zero concentration, (2) inadequate fractionation, and, most important of all, (3) the use of the intrinsically incorrect Staudinger equation for extrapolating far beyond the range of the cryoscopic measurements.

The much greater sensitivity of the osmotic pressure method permits its application up to molecular weights of about 1,000,000. Results obtained for higher fractions are insufficiently accurate for significant comparison with Equation (4). However, the good agreement obtained over the preceding two hundred-fold molecular weight range would seem to justify estimation of higher molecular weights by extrapolating the line in Figure 4. Under suitable conditions it is possible to synthesize polymers of isobutylene[35] having intrinsic viscosities as high as 10. The corresponding molecular weight calculated from (4) is about 10,000,000. So far as the author is aware there is no record in the literature of another synthetic (linear) polymer known to have a molecular weight approaching this figure. Polyisobutylenes of even higher intrinsic viscosity can be obtained by fractionation.

Viscosity average molecular weight.—Kraemer and Lansing[3] have shown that molecular weights of heterogeneous polymers calculated from intrinsic viscosities according to Staudinger's equation are weight averages. Since an equation of the form of (5) appears to be quite generally applicable to high polymer solutions, it is important to inquire concerning the type of average it yields. With Kraemer[36] we let $(\eta_r - 1)_i$ represent the viscosity increment of the i-th polymer component in the dilute solution. According to (5):

$$(\eta_r - 1)_i = Kc_iM_i^a$$

For the total viscosity increment:

$$(\eta_r - 1) = \sum_i (\eta_r - 1)_i = K\sum_i c_iM_i^a$$

$$[\eta] \equiv [(\eta_r - 1)/c]_{c=0} = K\sum_i w_iM_i^a/\sum_i w_i$$

since c_i is proportional to the weight fraction w_i of the i-th species in the polymer. Hence:

$$[\eta] = K\bar{M}_v^a \tag{5'}$$

where

$$\bar{M}_v = [\sum_i w_iM_i^a/\sum_i w_i]^{1/a} \tag{6}$$

or

$$\bar{M}_v = [\sum_i N_iM_i^{a+1}/\sum_i N_iM_i]^{1/a} \tag{6'}$$

where N_i is the number of molecules of molecular weight M_i.

The term "viscosity average molecular weight" seems obviously satisfactory for $\bar{M}_v$[37]. When $a = 1$, $\bar{M}_v$ becomes identical with the weight average $\bar{M}_w$ and (5) reduces to Staudinger's equation. When $0 < a < 1$, it can be shown that for a heterogeneous polymer $\bar{M}_n < \bar{M}_v < \bar{M}_w$. Consequently, the actual viscosity-molecular weight relationship (5) gives an average molecular weight somewhat nearer the number average determined osmotically than would be obtained if Staudinger's equation were to apply.

In comparing number average molecular weights with intrinsic viscosities, as in Figure 4, the heterogeneity of the samples obviously should be taken into account. Although all samples represented in Figure 4 were carefully fractionated, the distribution curves for the fractions unquestionably are much broader than the range of precipitating conditions would indicate. The fractions probably overlap one another to a very marked degree. In the absence of any definitive evidence concerning the heterogeneity of the fractions, rough estimates have been made of the ratio $\bar{M}_v/\bar{M}_n$ for $a = 0.64$ for various types of distributions, and in particular for distributions of the type predicted for fractionated materials by Schulz[15]. In this way it has been concluded tentatively that the viscosity averages for the fractions probably are no more than 10 per cent greater than their various number averages. On this basis the viscosity average molecular weight given by Equation (4) may be as much as 10 per cent too low. As there is no reason to expect variation in $\bar{M}_v/\bar{M}_n$ with the average molecular weight of the various fractions, the slope in Figure 3, and hence a in (5), probably have not been vitiated appreciably by the heterogeneity of the fractions.

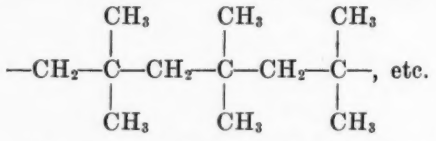
Structure of polyisobutylene in relation to viscosity.—That polyisobutylene molecules are strictly linear is indicated by the complete solubility in hydro-

carbons of even the highest molecular weight products obtainable. In general, an auxiliary process leading to random branching or cross-linking of the chains will cause partial insolubility if the process progresses far enough[38]. The extent of branching or cross-linking required for incipient insolubility when the chains are so long is exceedingly minute (of the order of one branch or cross-link per 500,000 units for the highest polymers). Consequently, appreciable deviation from linear polymer structure in the molecular weight range investigated experimentally is exceedingly unlikely. Staudinger's frequent contention[4] that deviation from Equation (1) is due to a branched structure cannot be applied in the present instance.

There is no evidence, such as Staudinger and Schulz[39] claim to have found in the case of polystyrene, for differences in polymer structure depending on the temperature or catalyst used in the preparation of the polymer. Fractions from polymers prepared in various ways (see Table I) fall on the same line in Figure 4. The relationship[40] between volume of precipitant and intrinsic viscosity (or molecular weight) is precisely the same for all polyisobutylenes investigated.

Finally, the divergence from Staudinger's equation cannot be attributed to the particular solvent, diisobutylene, in which the intrinsic viscosities have been measured. Preliminary comparisons of intrinsic viscosities in various solvents indicate lower intrinsic viscosities the poorer the solvent, in accordance with results for other polymers[41]. However, the ratio of the intrinsic viscosity in diisobutylene to that in another solvent is roughly independent of molecular weight. Thus, the slope of a plot such as is shown in Figure 4 is approximately independent of the solvent.

Both chemical[11] and x-ray evidence[42] support the plausible chain structure:



for polyisobutylene. Attempts to construct the space model show that severe interference exists between the methyl groups of successive units, leading to compression of the hydrogens well below their kinetic theory diameters[43]. Very probably this is the reason for the abnormally low heat of polymerization[11]. Possibly these interferences diminish the flexibility of the chains. Furthermore, the interferences are somewhat less for comparatively coiled-up configurations[44]. It should be expected, therefore, that the dimensions of the polyisobutylene molecule in solution probably are less than those of other polymers having the same number of carbon atoms in the chain. Intrinsic viscosities for polyisobutylenes should be correspondingly less than those for other polymers of the same chain length (contour length), according to current notions concerning polymer solution viscosities. That this is true can be shown by examination of results for rubber[7,42], hydrorubber[5] and polystyrene[39].

The present results fail to confirm the theoretical treatment of polymer solution viscosities advanced by Huggins[46]. Considering that the solvent molecules move through the essentially rigid chain structure of random configuration, Huggins arrived at linear dependence of intrinsic viscosity on chain length. Kuhn[47], on the other hand, considers that the solvent within the volume encompassed by the meandering chain moves with the chain. His calculations concerning chain configurations then lead to the conclusion that

the intrinsic viscosity should depend on a power of the chain length which, though greater than one-half, should be less than unity. The present results are consistent with this hypothesis.

The theoretical implications of the results presented here will be presented in greater detail in another publication.

Acknowledgment.—The author wishes to acknowledge the assistance of John Thomas and (Mrs.) M. D. Robbins in securing the experimental data.

SUMMARY

Experimental methods for fractionating polyisobutylene and for determining osmotic pressures have been described.

The ratio π/c of osmotic pressure to concentration has been found in the case of cyclohexane solutions of polyisobutylene to vary nonlinearly with concentration, contrary to recent theories advanced by Huggins and the writer. The slope of this relationship appears to be independent of molecular weight. Reliable methods for extrapolating π/c to $c = 0$ have been established, enabling the determination of absolute molecular weights with satisfactory precision up to values of about 1,000,000.

Molecular weights of polyisobutylenes calculated from Staudinger's equation are too low; the discrepancy is more than ten-fold at high molecular weights.

On the basis of data for carefully fractionated samples covering a two-hundred-fold molecular weight range, the intrinsic viscosity is found to be proportional to the 0.64 power of the molecular weight. This decided deviation from Staudinger's "law" cannot in this instance be attributed to nonlinear chain structure, as Staudinger has sought to do in other cases.

This dependence of molecular weight on intrinsic viscosity leads to the definition of a "viscosity average" molecular weight which is obtained when the relationship is applied to heterogeneous polymers. The viscosity average is less than the weight average molecular weight, which would be obtained if Staudinger's equation were applicable, and greater than the number average obtained by osmotic or cryoscopic methods.

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[22] Supplied through the courtesy of E. I. du Pont de Nemours and Co.
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MOTION PICTURE STUDY OF BALATA AND HEVEA LATICES

WITH OBSERVATIONS ON BUNA-S AND NEOPRENE LATICES *

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A previous paper[1] on ultraviolet microscopy of *Hevea* latex gave particle size data on two samples of commercial latex. From the photomicrographs it was possible to infer something about particle shapes and relationships.

Relative positions of particles as disclosed by the photomicrographs suggested that colloidal dispersions may be an orderly arrangement of particles controlled by forces acting between particles. The commonly held explanation of Brownian motion accounts for the motion of particles on the assumption of the molecular action of the liquid.

When these photographs were taken, Brownian motion had been arrested by diluting the latex with salt solution. Ultraviolet microscopy required an exposure interval of about 30 seconds. After a slide was prepared, it was necessary to wait for the motions to cease before an exposure was taken. The particles gradually slowed down and, when motion stopped, they seemed to be in positions which indicated some sort of relation between particles.

Certain particle relationships apparently prevailed as follows:

1. An arrangement of small particles in straight or curved lines. Sometimes there is a gradation in the size of the particles forming the line—a large particle at one end and a gradual diminution in particle size toward the other end. In the photomicrographs, the larger particles do not appear to be similarly arranged in lines, but this is believed to be due to the fact that dilution of the latex has resulted in few large particles being present in a field, obscuring the effect. Other investigators have reported this line arrangement of particles.
2. A doublet consisting of two particles, one larger than the other, associated as a unit. So common is this unit that one can scarcely touch a pencil point to one of the photomicrographs without blindly pointing to a doublet. The smaller particle sometimes appears in contact with the larger particle, but generally the two are separated. The larger particle is called a "primary particle", the smaller particle, a "satellite".
3. An occasional group consisting of three particles of about equal size arranged in the form of an equilateral triangle.
4. An occasional group consisting of four particles of about equal size arranged in the form of a rectangle.

Instantaneous photomicrography would be required to determine whether the particle arrangements shown by the ultraviolet plates actually exist when the particles are in Brownian motion.

Precision motion picture apparatus suitable for colloidal dispersions was not available. The design of such apparatus was studied, but before undertaking assembly and construction, a preliminary investigation was made with

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 34, No. 11, pages 1371–1381, November 1942. A section which itemizes the features of several thousand feet of film is omitted.

improvised apparatus consisting of a dark-field (cardioid type) ultramicroscope associated with a roll-film photomicrographic camera.

An attempt was made to use the conventional dark-field cells or chambers to provide a suitable film of the diluted latex for microscopic investigation. These devices proved unsatisfactory. Evaporation of the fluid from the edges of the cell introduced streaming and flowing of the particles and rendered observations on particle motions worthless. Before proceeding further, it was necessary to work out an entirely different type of mount and one which could be sealed hermetically.

PREPARATION OF SLIDES

The final arrangement adopted and the procedure for making the slides of latex consisted of a modification of the practice previously reported for ultraviolet microscopic examination of latex. Standard glass slides and cover slips of suitable thickness were employed. They were carefully selected for quality. Slides and covers were first washed with soap and water. They were then cleaned in hot sulfuric acid and potassium dichromate solution, rinsed in hot running water, flushed with distilled water, flushed with absolute ethyl alcohol, drained momentarily, and then flashed through a Bunsen burner to ignite and burn the alcohol. If properly carried out, this procedure results in clean slides and slips.

About 3 to 5 cc. of ammonia solution (pH 11.5) were placed in a small glass-stoppered bottle, and to this was added from one to several drops of latex to secure the desired dilution. This solution was stirred, and a small drop placed on a cover slip.

The slip was quickly lowered to a slide mounted on a turntable. The latex solution spread to a film by the weight of the cover slip. A piece of bibulous paper was placed over the cover slip and gently pressed downward. Any excess solution exuding about the slip was taken up by the paper. The slide was centered on the turntable, and the cover slip sealed to the slide by means of a sable brush dipped in a mixture containing equal parts of vaseline and olive oil. Sealing was accomplished in the usual manner by spinning the turntable and ringing the cover and slide. This method provides an airtight and leakproof seal. An average thickness for the latex film is 10 microns.

PRELIMINARY INVESTIGATION

In the preliminary study, a dilute solution of latex was prepared and a slide made. A doublet was brought to the center of the field. The particles were in motion, but they did not migrate from the center of the field. Once centered, they remained indefinitely in their approximate positions. A series of fifteen instantaneous photographs was taken of the doublet. Nearby was a large stationary particle; it served to show the relative motions of the two particles comprising this doublet. A time interval of about 4 seconds elapsed from one exposure to the next.

Figure 1 is a diagram made by projecting the fifteen exposures on a screen at a fixed position and drawing the outlines of the particles. Particle movements actually are in three dimensions, but in this diagram the movements are reduced to a single plane. It seems obvious that the particles approach and recede from one another, and that the smaller particle moves about the larger one.

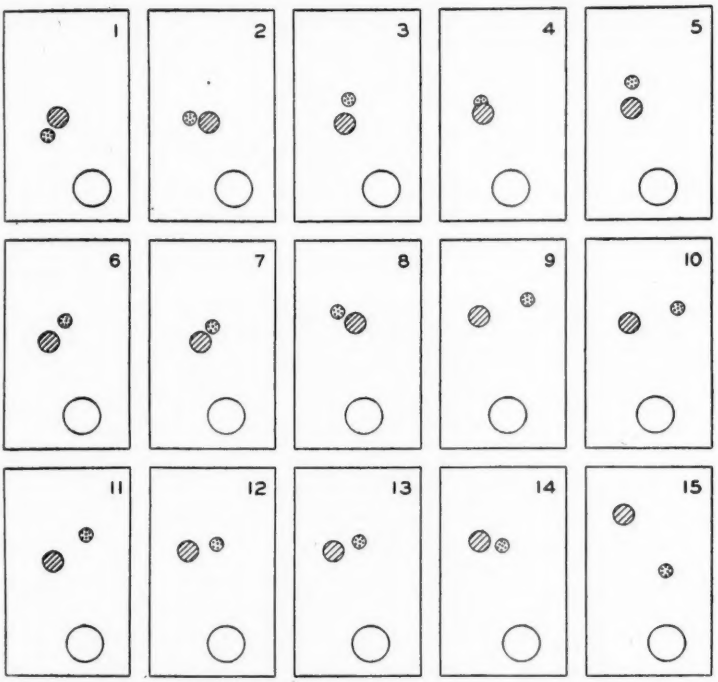


FIG. 1.—Motions of a doublet.

Figure 2 is of another slide with many particles present. Two instantaneous photomicrographs are shown of the same field, with a time interval of approximately 4 seconds between exposures. Lines of particles or chains are visible in each photograph. The particles were in active Brownian motion

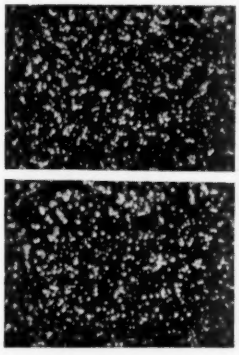


FIG. 2.—Two instantaneous micrographs of same field, showing chains.

when these photographs were taken. Individual particles did not migrate out of the field except an occasional particle at the border of the field. The particles approached and receded from one another, but never seemed to hit or make contact. In each photograph there are dark areas of about the same

shape, and in the same location, which are practically devoid of particles. Some combination of circumstances tends to keep the particles grouped, and while they are actively motile in the Brownian sense, they do not migrate or disperse to form a completely uniform field.

MOTION PICTURE APPARATUS

Precision motion-picture equipment was built by combining the best microscopic, optical, and photographic apparatus (Figure 3). There are two sources of light: an automatic arc-lamp system operating from a specially designed

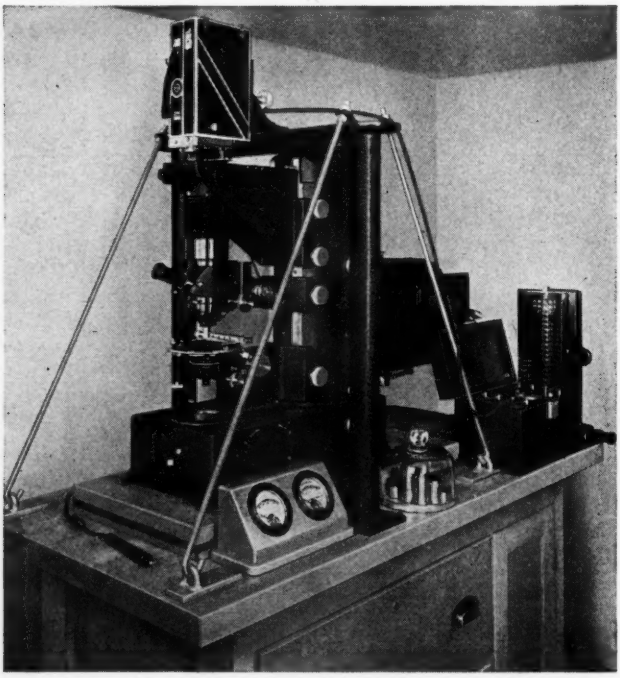


FIG. 3.—Motion picture apparatus.

motor generator set (not shown) and a separate incandescent lamp system. The arc-lamp system is used for most of the photographic work, while the incandescent lamp system is used for preliminary or visual examinations.

The motion picture camera is the Ciné Kodak Special. It is electrically operated, and diversified control of the equipment is assured. The camera is mounted on a welded bridge of substantial construction, which is insulated from the microscope. A beam splitter is employed so that the image may be under constant observation.

The conventional dark field condenser may be used, or the color-differential illuminating system originally devised by Rheinberg[2]. The use of the color-differential system in this apparatus has been perfected and applied to colloidal phenomena.

It allows practically the whole cone of light to be utilized, and is more efficient than the conventional dark field. Because of this increased efficiency, it is possible to record the colored images on Kodachrome film. Color contrasts and sharp definition are attained, and the grainless nature of Kodachrome film is utilized. When the index of refraction of the dispersed phase is close to that of the dispersing medium, the color-differential system in its present state of development is not so effective as conventional dark field methods. It is possible also to resolve smaller particles with dark field than with the color-differential system. Balata and *Hevea* latices are well suited to the color-differential system, but synthetic latices, such as Neoprene and

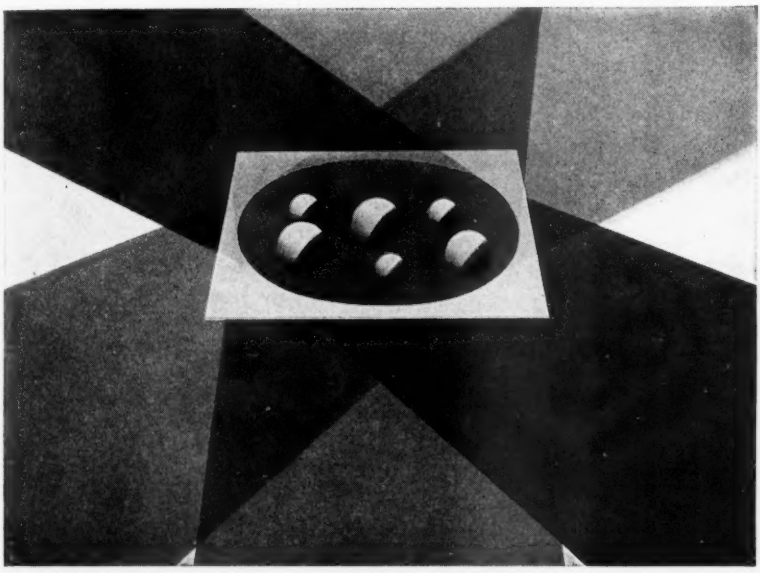


FIG. 4.—Rheinberg color-differential system.

Buna-S, are not well resolved except by dark field. Improvements in apparatus and technique may overcome this difficulty.

The color system reveals the particles in color against a field of complementary color. Various color combinations may be used. When motions of individual particles or small groups are to be analyzed, it is advantageous to use a three-color system. One side of the object is illuminated with red light, the opposite side with green light, and the field with blue light. Symmetrical coloring of particles results. The same sides of all particles are then colored red, the opposite sides are colored green, and the red-green particles are seen against a blue field. A schematic diagram of the illumination system appears in Figure 4. Figure 5 shows the particles as viewed through the microscope or as recorded on Kodachrome film. (Present reproductions from the films are of necessity in black and white.)

When a satellite gyrates about a primary particle, this symmetrical coloring causes red to be superimposed on green as the particles cross. When the films are projected, it can be seen whether the satellite passes over or under the

primary particle. The three-color system also results in better definition by introducing the third dimension, depth. A spherical particle looks spherical. Pear- and tear-shaped particles, merging particles, or particles in masses, the result of creaming or agglomeration, are seen sharply defined and in three dimensions.

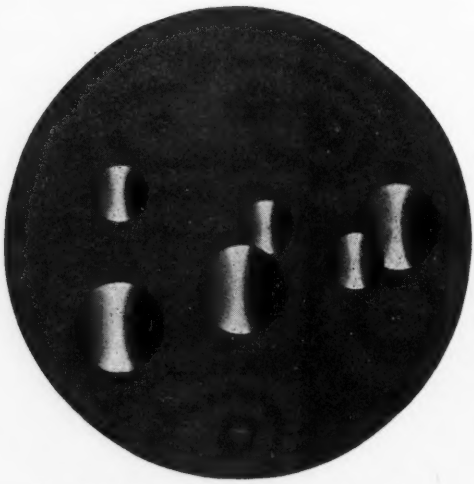


FIG. 5.—Appearance of particles by color systems.

A color filter combination often can be selected that will take advantage of the absorption or reflection characteristics of the material under examination and further assist in developing contrast

GROUPINGS OF PARTICLES AND CHAIN FORMATION

To study grouping and chain formation of particles, balata latex was diluted with ammonia solution (pH 11.5) as previously described. Using the color-differential system for illumination and a magnification at the film of 25 to 50 times, the chains could be observed forming, breaking up, and reforming. Hundreds of feet of film have been taken and the results studied. The color contrast between the particles and the background proves to be of great help in the motion studies.

There is an unmistakable tendency for the particles to arrange themselves in ever-changing patterns. It is also apparent that the dispersion has numerous areas almost devoid of particles except for a few smaller ones. These vacant areas or "holes" change slowly in location, shape, and size.

This structural arrangement into chains and groups of particles in Brownian motion and the interspaces is readily visible at low magnifications in such dispersions as balata and *Hevea* latices, and in many other organic and inorganic dispersions. It can be seen to best advantage with the color-differential system, but can also be seen with dark field. It seems likely that all colloidal dispersions manifest this same structural arrangement and that the phenomenon may be the result of forces acting between particles. As long as the particles are in Brownian motion, the pattern is ever changing. Chains, whorls, and an arrangement suggestive of dendrites are continually forming and breaking up.

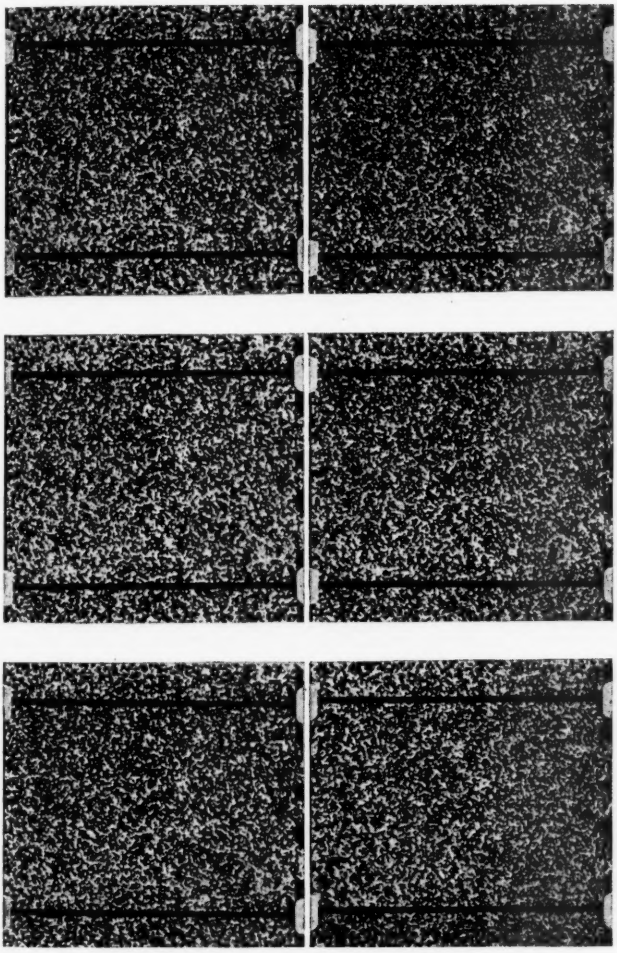


FIG. 6.—Six typical frames showing chains.

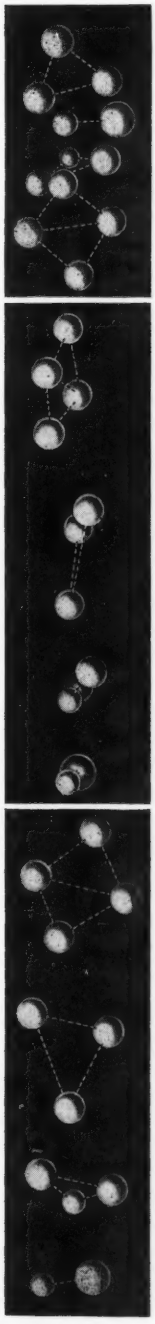


FIG. 7.—Diagrams of simple units.

Figure 6 shows six typical frames, taken at equally spaced intervals from one of the films. The resolving power and the magnification are purposely low, so only aggregations of particles are readily seen with the eye. Individual particles are resolved and can be seen by close inspection of the projected film. All the particles are in Brownian motion. The particles do not migrate, so the particles in any one frame are the identical particles shown in every other frame. A few border particles may move in and out of the frame, but otherwise all six frames are identical except for the pattern which has changed.

Similar experiments performed with preparations of *Hevea* latex show no distinguishing differences except that the *Hevea* particles are smaller than the balata particles and the motion is a little faster.

By taking the film at two or four frames a second instead of sixteen frames, fast-action pictures are secured when the film is projected at the normal rate of sixteen frames per second. In these films the pattern forms and breaks up quickly, and the action can be followed. When taken and projected at normal speed, the action is gradual, and one pattern slowly fades into another.

This characteristic of forming chains and groups seems to be as inherent in the nature of the colloidal solution as is the Brownian motion.

SIMPLE UNITS OF COLLOIDAL STRUCTURE

Since the layer of liquid containing the particles of rubber in Brownian motion is about 10μ thick, the motions of the particles are in three dimensions. It has been shown that in *Hevea* latex only about 10 per cent of the particles are larger than 0.50 micron. In balata the percentage would be greater. In a film 10 microns thick, freedom of motion is alloted the particles.

The simple units of colloidal structure are represented by the models reproduced in Figure 7. The left-hand picture illustrates what might be termed "a plan view of simple elements". If this arrangement of models is turned over 90°, the same assembly looks quite different, as shown in the middle row. A regrouping and bunching of the models results in the wider and shorter band at the right. It is suspected that, due to forces acting between particles, simple units of structure orient themselves into chains and groups much in the fashion shown by the models.

Motion picture studies show that a primary particle may have more than one satellite, and that a satellite itself may have a still smaller particle as its satellite. Very small particles are faster-moving than larger particles, and motion studies show that very small particles are not necessarily held bound by large particles. They may, and generally do, gyrate about a primary particle momentarily, then pass rapidly to another particle where the gyrations are repeated, and so on. They do not migrate or pass from the field of view, but move about from one particle to another. When a small particle encounters another small particle, they may gyrate momentarily and pass on.

As the magnification is increased, motion as well as particle size is magnified. At high magnifications the smaller particles appear to be dashing about in a zigzag fashion. Most of this erratic and jerky motion seems to be due to inability to stop the motion optically rather than to any inherent characteristics of the particles themselves. When the particles are recorded at lesser magnifications, the jerky motions are subdued or ironed out altogether. At moderate magnifications sufficient to resolve the particles, a clearer concept is obtained of particle relations and the motions occurring.

The resolving power when the color-differential system is used with low-aperture dry objectives is sufficient to resolve both balata and *Hevea* latices without difficulty. To secure detail of individual particles, such as merging particles, it is necessary to employ the best oil immersion objectives. Special objectives for this purpose were procured.

The technique for color-differential illumination may be used successfully at high magnifications, but it is not possible to photograph in color at a normal speed of sixteen frames. Kodachrome film is not sensitive enough. Motion of the larger particles, however, can be stopped by an automatic time exposure of ¼ second, and this is the procedure followed for detail studies. When such a film is projected at sixteen frames per second, the rate of motion of the particle is four times normal.

The smaller particles in the field do not have definite shape when photographed by automatic time exposures. Their motion is not stopped. They dart wildly about like miniature leaves blown by a gale. Photographed at lower magnifications and at normal speed, their motions are regular and orderly. They behave similarly to the larger particles except that they move faster and change partners more readily and more often.

The smaller particles in balata and *Hevea* latices are on the border line of particle dimensions which at present can be resolved with the color-differential method of illumination. Synthetic latices are composed of still smaller particles, with little variation in particle size. To record these particles requires dark-field methods, high-resolving-power immersion objectives, and high-sensitivity film.

In synthetic rubber dispersions (Neoprene and Buna-S, for example) the particles move at a high rate of speed; they change partners, they seem to form groups and chains, and dark interspaces or "holes" are visible in a shifting pattern. The particles do not migrate out of the field.

DISPERSIONS

Dilute dispersions.—Very dilute dispersions of both balata and *Hevea* latices were filmed with the object of studying individual particle motions and inter-particle relations. A single, freely suspended particle manifests very little motion and seems to represent a state of colloidal equilibrium. The film shows that the nearest particle is distant about seventy times the diameter of the isolated particle. It may be that such distant particles influence one another.

An isolated doublet moves only slightly, about the same as a single particle. The satellite slowly approaches and recedes from the primary particle and gyrates about it. The individual component particles of isolated triplets and quads also move or sway slowly. They seem to retain their approximate relation to one another.

More concentrated dispersions.—As the concentration of the latex is increased, particle motions seem to increase in rate of speed. With few particles in the field, motions are slightly perceptible. When many particles are present, the activity seems greatly increased. A typical latex, in this case balata, is reproduced from the films (much enlarged) in Figure 8.

COMPARISON OF LATICES

Two latices may be compared by "splitting" the film. To accomplish this, paired screening masks are used. With one side of the frame blocked off by a mask, balata latex was filmed on the exposed side. The film was rewound,

the half mask removed, and the opposite half mask inserted to cover the exposed film. *Hevea* latex was then filmed on the unexposed side. When projected, the two latices are seen side by side. The distinguishing differences are a relatively smaller particle size and a slightly faster motion for the *Hevea* latex.

When *Hevea* latex and a synthetic latex are filmed together, the structural differences are apparent. The synthetic latex is uniform in size, and its motion

FIG. 8.—Typical latex, balata, much enlarged from the films.

is much more rapid. If the synthetic latex is correctly exposed, *Hevea* latex, with identical exposure, will be overexposed. Halation and scattering of light will be the result.

This comparison feature of motion picture photomicrography provides convincing evidence, not only on particle size range but on degree of agglomeration, stability of the dispersion, effects of various additive substances, changes in speed with changes in pH approaching the isoelectric point, creaming, etc. Figure 9 is reproduced from the comparison film showing balata and *Hevea* latices.

TIME STUDIES OF PARTICLE SHAPES

As stated in the earlier paper, the predominant shape of the rubber latex particle is spherical. The evidence from these motion picture films seems unmistakable. This does not mean, however, that irregularly shaped particles are not present. The same specimen of *Hevea* latex, kept in a platinum crucible, sealed with a platinum cover, and stored in a refrigerator for over a year, has

FIG. 9.—Comparison films of balata and *Hevea* latices.

been examined periodically. The shape and size of the particles undergo change.

Fresh latices seem to have a preponderance of spherical particles. As the age of the latex increases, more irregular-shaped and large spherical particles are seen. The irregular-shaped particles result from two or more particles becoming attached to each other and then merging so that the outlines of the component particles gradually disappear; a pear-, tear-, or egg-shaped particle results. As the merging process continues, the irregular-shaped particle becomes spherical.

This cycle of events, resulting in the merging of two or more particles to form a single large spherical particle, may take place in a few seconds. It may occur much as two drops of water combine quickly to form a single larger drop. Generally the merging occurs slowly, a matter of hours. Sometimes it continues for a while, then the merging apparently ceases, and observations over many hours show no further changes.

Figure 10 shows various merging and irregular-shaped particles (enlarged from the film). Two or more particles may become attached to a larger particle. A common form is a chain of particles with a large particle at one end and a gradual decrement in the size of the particles toward the other end.

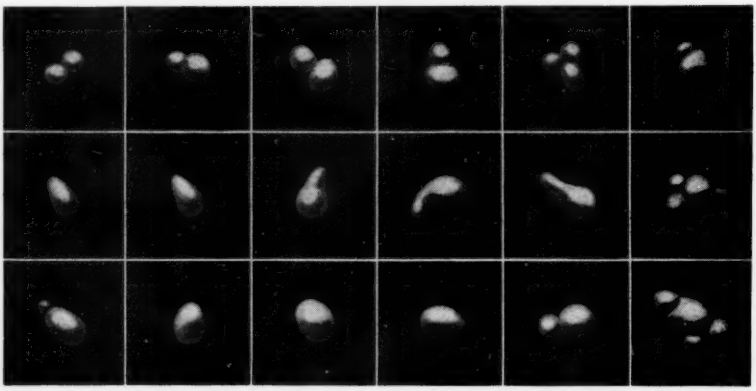


FIG. 10.—Merging and irregular-shaped particles.

If such a chain is kept under observation and filmed at intervals, the merging process, which results in a single large spherical particle, may be seen as it occurs. Such a time study forms a part of the film record on which this article is based.

Figure 11 shows some progressive stages in a time study of merging *Hevea* particles. It is reproduced much enlarged from the motion picture film. The sequence of events appears as follows:

1. Two or more particles become attached; common arrangement is a large particle with attached smaller particles forming a tapering chain.
2. Attached particles show evidences of being pulled into the large particle.
3. Spherical outlines of the smaller particles disappear, forming a pear-shaped particle.
4. The neck is pulled into the bulb, forming an egg-shaped particle.
5. The egg-shaped particle becomes spherical.

The time interval represented by *a* to *p* (Figure 11) is 26 hours. The particle was continued under observation for another 30 days, but no further change occurred. The last film sequence was taken on the twentieth day.

This time study indicates that *Hevea* latex probably is composed originally of small spherical particles. Some of these particles become attached and form groups or chains. The smaller particles are gradually merged, their outlines disappear, and, if the process continues, a spherical particle ultimately results. In older latices irregular-shaped and large spherical particles are more numerous, as previously stated.

Very fresh latex may be composed mostly of small spherical particles, with few merging particles. No opportunity has been afforded to examine such a latex. As the latex becomes older, the number of merging particles increases. Particle-size data must show a shift in the particle-size distribution curve toward the larger sizes with increase in age of the latex.

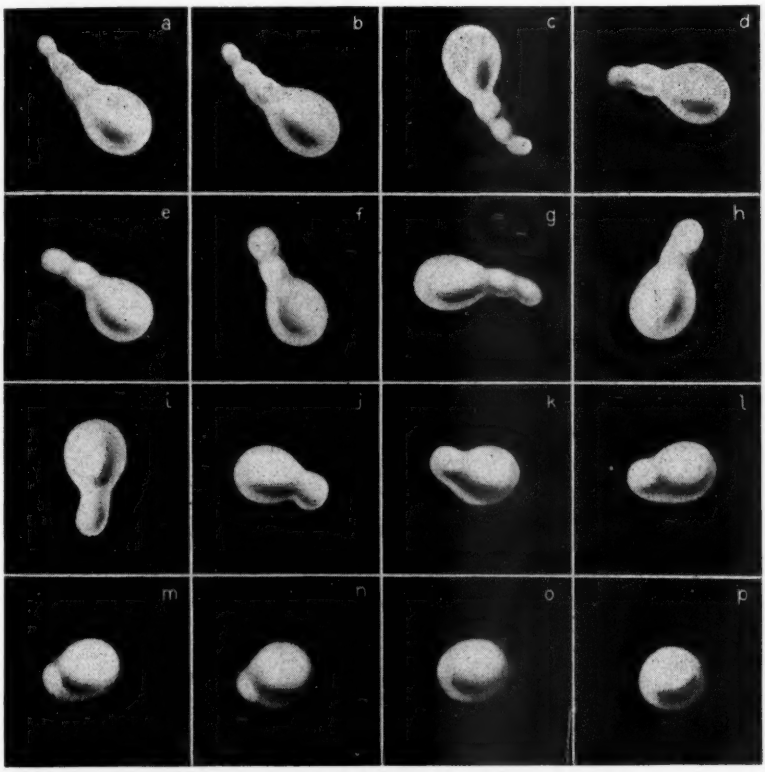


FIG. 11.—Time study of merging *Hevea* particles.

ELECTRICAL EFFECTS

Special types of cells were designed so that the effect of electrical potential could be followed on dispersed particles of balata latex in Brownian motion. Experiments were first made with available types of cells, but these proved unsatisfactory.

The cells could not be tightly sealed, and streaming and flowing of the particles occurred. The cells were clumsy to assemble, and the electrical connections were insecure. Some required specially corrected objectives because of thick quartz cover slips. This seriously limited experimental procedure.

The final form of the cell employed consisted of a 1 × 3 inch polished glass slide, 0.90 mm. thick. This slide was drilled for two platinum or silver electrodes. The electrodes were 3 mm. in diameter, and were mounted 30 mm. apart. The surface of each electrode was mounted flush with the surface of

the slide and secured by threaded fastenings on the under side. Very flexible stranded wires were attached to the fastenings for the purpose of making electrical connections. A rectangular cover slip, 22 × 40 mm., was used, and the slide was prepared as previously described. In these experiments particles are shown in Brownian motion. Electrical potential is then applied.

At low magnification, migration appears in two distinct layers, one moving faster than the other. One layer appears to be along the slide and the other along the cover slip. Chains and groups are seen with the changing pattern as previously described. On application of electrical potential, these patterns

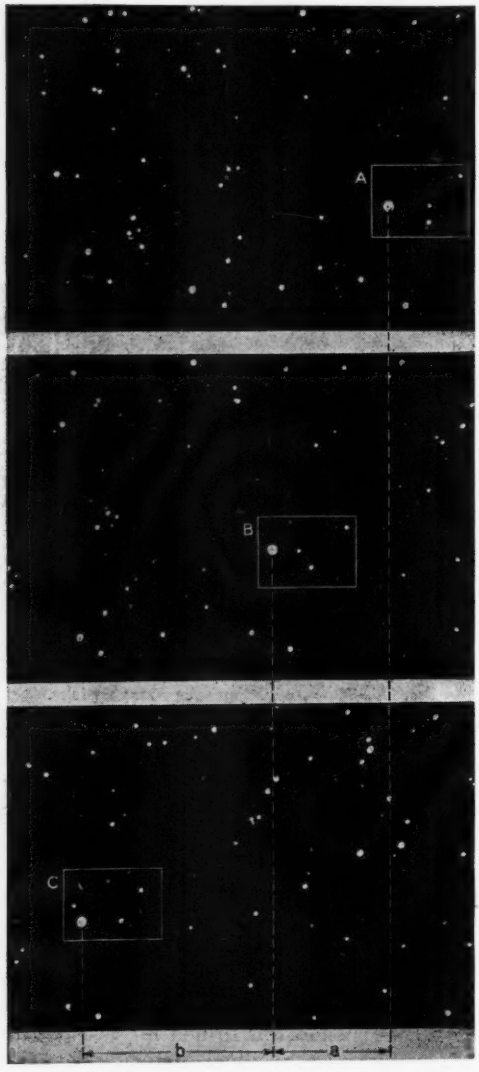


FIG. 12.—Enlarged reproduction of three frames showing electrical effects.

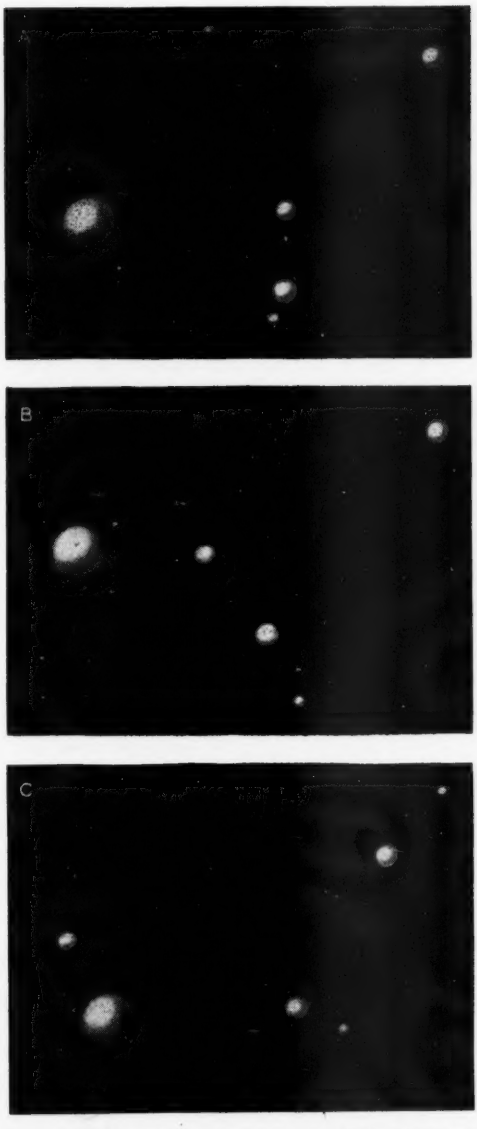


FIG. 13.—Enlarged reproductions of one constellation from Fig. 12.

are not broken up and destroyed, but continue to form and change in a normal manner as they drift across the field toward the anode. At high magnifications and with three-color illumination, the behavior of individual particles and structural units can be observed.

It appears that the application of electrical potential does not materially alter the interrelations of dispersed particles in Brownian motion. A doublet travels as a unit, with the satellite gyrating about the primary particle. The triplets and quads travel as units. Migration to the anode is at a uniform

rate, regardless of particle size; large and small particles travel at the same rate. Sometimes a satellite in its gyrations about a primary particle is moving against the direction of migration, sometimes across the current, and sometimes with the current. Study of the films seems to show that migration to the anode has little if any effect on the Brownian motion, regardless of direction.

Figure 12 consists of three frames, enlarged photographically from an electrical sequence of the films. The same constellation of particles in each is enclosed by a rectangle. This figure is intended to show the movement of a particular constellation to the anode.

Figure 13 represents an enlargement of the constellation so that the motions of the individual particles in relation to one another can be seen more clearly. The large primary particle which appears to dominate the constellation has three satellites and each satellite has a satellite of its own. When potential is applied, the effect is to move the constellation as a whole from *A* to *B* to *C* toward the anode.

FREQUENCY GRAPH OF *HEVEA* LATEX

Hevea latex is composed of particles with a wide spread in particle size, ranging from about 0.10 to 2.0 microns in diameter. The particle size data of the earlier paper[1] (Tables I and II) were replotted to show the frequency with which the various sizes occur (Figure 14).

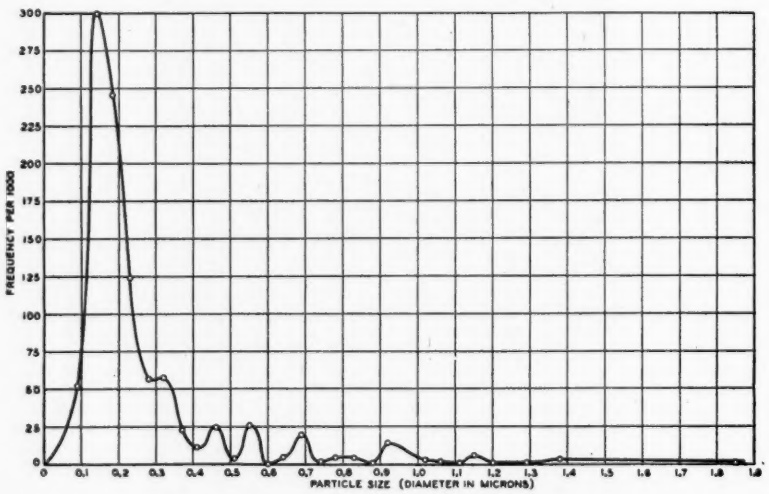


FIG. 14.—Frequency chart of *Hevea* latex.

About 75 per cent of the particles are smaller than 0.30 micron, but in the 25 per cent of the particles which are larger is contained the greater mass. The larger particles are the primary particles, the smaller particles are the satellites. That portion of the particles represented in the chart by the range from about 0.30 to 1.85 microns are the particles which, according to the motion pictures, seem to have strong interparticle relationships. That portion of the particles represented by the cusp are the particles of weaker relationships.

Since it is now clear that the larger particles do form from the merging of two or more smaller particles, the speculation appears permissible as to whether

or not, in its early history, *Hevea* latex may not be predominately of the character represented by the cusp. No opportunity has been afforded to examine a latex as it emerges from the tree; perhaps if this had been done, merging might have commenced and larger particles resulted. Observations show that a single large particle can develop in a matter of seconds, or it may take place in hours or days.

Lacking as yet precise mathematical data on particle sizes of synthetic latices, a frequency chart cannot be drawn, but from the films it appears to be a cusp similar to the left-hand end of Figure 14 but disposed somewhat farther to the left.

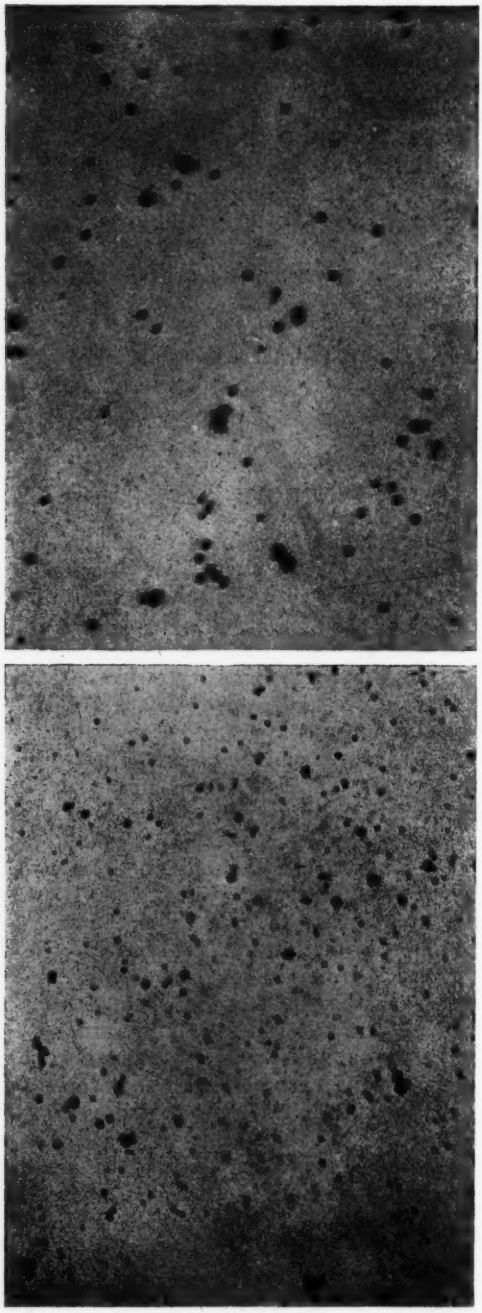
In this connection it may be permissible to speculate further as to whether the practice of rubber technology has demonstrated large or small particle sizes to be desirable. If a small size is beneficial, and one might think this to be the case, then man-made latices have achieved surprising results and uniformity in that direction. Apparently these synthetic latices undergo the same particle merging and growth as *Hevea* latex, but work to date does not warrant an elaboration of this observation.

SYNTHETIC LATICES

Neoprene and Buna-S latices have been studied to some extent as a preliminary survey. They show great similarities in colloidal structure. Some preliminary attempts were made to determine particle size range. The particles of each latex are transparent to ultraviolet light, but could be stained sufficiently with methylene blue to be made visible by photography with the ultraviolet microscope. Considerable agglomeration occurred, and results are of doubtful value. More work is required before a reliable frequency curve can be produced. Measurements made from projected images of the films seem to indicate that a cusp lies between 0.05 and 0.25 micron. All of these small particles appear to be spherical. Each latex contains some larger and irregular-shaped particles and small group agglomerates. Some of the larger particles are pear-shaped. When these synthetic latices are examined by the color-differential method of illumination, the only particles which can be seen are the larger irregularly shaped ones and small groups.

Dilution of Neoprene latex to the point where individual particle motions could be followed apparently disclosed a light sensitivity effect. The particles quickly fade. If the stage is moved to a new location, the particles are first brilliantly illuminated and then quickly fade.

The particle size of synthetic latices is much smaller and more uniform than *Hevea* latex. Of the samples examined, Buna-S latex appears definitely smaller in particle size than Neoprene latex. Brownian motion of synthetic latices is faster than the *Hevea* latex. The particles seem to form chains and groups, with dark interspaces in the same manner as balata and *Hevea* latices, but the pattern changes with greater rapidity. The small particles appear to have the same interparticle relations as are found among the smaller particles of *Hevea*. When the Brownian motion gradually ceases, doublet formations are common. In active Brownian motion the doublet formation is transitory, as the particles seem similar in their behavior to the small particles of *Hevea* which are constantly "changing partners". Structurally the synthetic latices are similar to *Hevea* latex, but with the larger particles screened out.



B. ×88,000

A. × 33,000

FIG. 15.—Electron micrographs of colloidal gold.

COLLOIDAL GOLD

That doublet formation is a fundamental element of colloidal structure and wholly independent of the nature of the dispersion seems to be established by Figure 15. These electron micrographs show that the doublet (two particles, one slightly larger than the other) prevails in colloidal gold dispersions. In Figure 15*A* many triplets can be seen also. Barnes and Burton[3] estimated the colloidal gold particle as 125 Å. in diameter.

CONCLUSIONS

In dispersions of *Hevea* or balata latex, motion of the particles appears to be controlled by forces acting between particles.

The particles are known to have negative charges. It is believed that these charges may not be uniformly distributed over the surface of the particles, and that they fluctuate in intensity. The charges tend to keep the particles separated. Under normal conditions of motion there is no evidence that the particles collide. They approach and recede from one another. Particles differing in size are found associated. A common unit is the doublet, composed of a large particle and an associated small particle acting as a satellite. Particles of varying size seem to have a tendency to form a group or constellation. The motions of a constellation appear to be centered about the largest particle. This particle may have several satellites. Each satellite may have one or more satellites. A large particle is never seen to gyrate about a smaller particle.

If the negative charges are nullified, agglomeration takes place. There seems to be some force acting in opposition to that of electrical repulsion.

Isolated single particles or units (doublets, triplets, and quads) seem to manifest very little motion. As the concentration of the dispersed particles is increased, the motions appear to be greatly increased. Mathematical analyses based on measurements of the films should provide data which will determine whether this assumption is valid.

In dilute dispersions, particle relations can be readily demonstrated, and the particles seem to assume a state of colloidal equilibrium. It appears that the particles were mutually in a state of tension. Motions are slight.

Rather concentrated dispersions form chains, groups, and dark interspaces or "holes". No evidence has been deduced that magnetism plays any part in this grouping arrangement. It is believed that the phenomenon may be fully accounted for on the basis that it is the resultant of forces acting between particles.

Time studies show that merging of particles occurs. A simple case may be described as two spherical particles, one larger than the other, in doublet arrangement. The smaller particle may lose its charge, or through some other cause is attracted by the larger particle to which it becomes attached. Through the action of other forces, it appears to be pulled into the larger particle, resulting in an irregularly shaped particle. Ultimately, under favorable conditions, the larger particle completely absorbs the smaller particle and then becomes spherical. During the merging process, however, other particles may be attracted and become attached to this irregular-shaped particle.

A common arrangement seems to be a tapering chain of particles, consisting of a large bulbous particle at one end to which have become attached several particles, each succeeding particle somewhat smaller in diameter than its neighbor. In process of merging, these particles are gradually pulled into the large bulbous particle, which ultimately may become a large spherical particle.

Experiments show that the application of a potential causes the particles to migrate to the anode, a fact which has been established for some time. In the migration of the particles to the anode, the interparticle relations are not affected by the application of potential. Simple units of colloidal structure travel as individual groups; this seems to show that the forces which cause the particles to arrange themselves in groups or chains are in no way related to the forces inducing the migration to the anode.

The very small particles of *Hevea* latex, or dispersions of Neoprene or Buna-S latices, in which a very small particle size prevails, behave in many respects the same as do the assorted larger particles of *Hevea*. They form simple units and chains, with resulting interspaces or dark "holes". The interparticle relations are weaker and more transitory. The particles "change partners" readily. If Brownian motion is allowed to subside gradually, the simple units of structure are found existing in the settled particles. This same arrangement has been found in electron micrographs of colloidal gold, the particle size of which has been estimated at 125 Å. in diameter.

ACKNOWLEDGMENT

The author is indebted to A. R. Kemp and W. G. Straitiff of Bell Telephone Laboratories, who have supplied the specimens required and for suggestions and criticisms. He is also indebted to the American Cyanamid Company for making available the electron micrographs of Figure 15.

The films have been shown privately on occasions to interested scientists for the benefit of comments and criticism. To all of these I wish to express my gratitude and appreciation. Among them I wish particularly to mention William H. Ordway and G. S. Pesquera, Metropolitan Life Insurance Sanatorium; Henry B. Allen and associates of the Franklin Institute; J. F. Mahoney and R. C. Arnold, the U. S. Public Health Service; C. E. K. Mees, Eastman Kodak Company; Edward Mallinckrodt, Mallinckrodt Chemical Works; Arthur B. Lamb and R. W. Hickman, Harvard University; and H. Bowling Barnes, Charles J. Burton, and T. G. Rochow, American Cyanamid Company.

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ELECTRODECANTATION FOR CONCENTRATING AND PURIFYING LATEX*

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DUNLOP RUBBER CO., FORT DUNLOP, BIRMINGHAM, ENGLAND

The chief methods employed in the production of concentrated latex have been confined to the controlled evaporation of water from the latex by the application of heat, concentration by centrifuging, and separation of the latex into layers of different concentrations by the action of creaming agents.

Recently, another process has been used commercially, which produces concentrates similar to those obtained by the centrifuging and creaming methods in that a substantial part of the serum constituents is removed during the concentration.

The new method is based on phenomena observed by Pauli and his coworkers[1] on the behavior of colloidal sols when subjected to electrodialysis. It was noted that in the purification of sols, such as silicic acid and serum albumen, by subjecting them to electrodialysis between vertical semipermeable membranes, separation was frequently obtained into superimposed layers containing different concentrations of the sol. The more concentrated layers were uppermost, or vice-versa, according to the relative densities of the sol and dispersing medium. This stratification is probably the result of the combined influence of the electrical potential and gravitational force under suitably chosen conditions. The colloidal particles migrate to one of the membranes under the influence of the electric field, with consequent concentration at the membrane surface. If the field strength is not too great, the particles become more under the influence of gravitational force than of the electrical force, tending to cause deposition on the membrane. The concentrated layer of particles tends, therefore, to move upwards or downwards along the surface of the membrane in accordance with its relative density with respect to that of the surrounding liquid. Conversely, there is a corresponding reduction in the concentration of the sol at the other membrane surface, which promotes a flow of more dilute dispersion in the opposite direction to that of the stream on the other membrane. If this action is allowed to continue, the dispersions of different concentrations spread out through the cell liquid in the form of horizontal layers which may be decanted.

Pauli and Stamberger[2] studied the behavior of aqueous dispersions of rubber under these conditions. Thick depositions can be obtained on the anode when latex is subjected to electrophoresis, or on the semipermeable walls of a cell containing the anode and a suitable electrolyte. In such cases the electrical potential must be high enough to urge the particles to the anode surface with sufficient force so that any gravitational action on them is substantially overcome.

It was found, however, that, by adjustment of the electrical potential and concentration of the latex, deposition of the accumulating particles on a semipermeable membrane surrounding the anode could be prevented. Because of its lower density, the concentrated layer was therefore free to move upwards

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along the membrane wall under the influence of gravity. The layer near the cathode became less concentrated and, therefore, more dense than the surrounding latex, which caused it to move in a downward stream. Separation of the latex into two layers was thus obtained, in which the bulk of the rubber particles were present in the upper layer.

The efficiency and rate of concentration of latex in the upper layer depends mainly on the initial concentration of the latex and the electrical potential applied. In general, the lower the initial concentration and the potential employed, the more efficient is the separation. The speed of layer formation is, however, progressively reduced.

A continuous range of concentrations and field strengths can be chosen between the extremes of almost complete stratification and of complete deposition on the membrane surface in which both phenomena take place in relatively

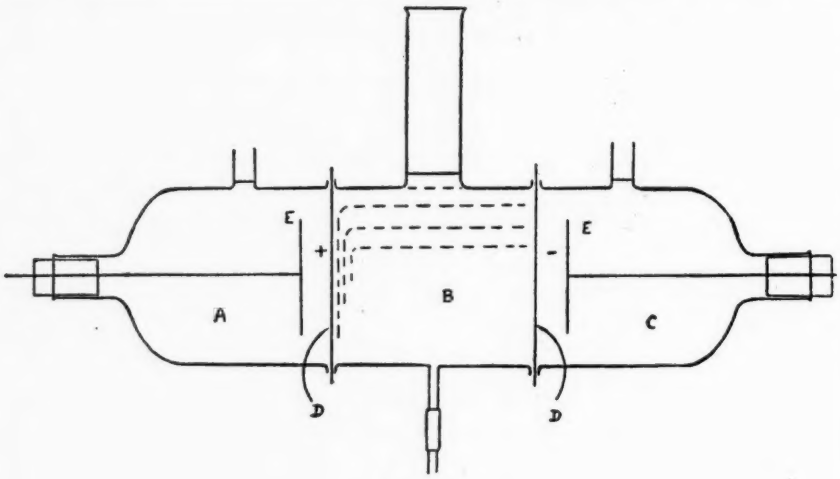

FIG. 1.

varying degree. Particles deposited on the membrane represent a loss of rubber as far as the yield of concentrate is concerned, and the efficiency of the membrane is also reduced. It was found, however, that potentials which would normally cause some formation of deposit could be employed by reversing the current periodically during the process. In this way the rate of separation could be increased without the attendant disadvantage of membrane deposition.

Providing that the field strength is not too great, any latex particles deposited on the membrane are still in a reversible state and are, therefore, returned to the disperse phase when the current is reversed. The membrane is thus freed during the inversion period from deposit, while the upward separation proceeds along the clean surface of the other membrane. By periodically reversing the current in this manner, the separating process may continue for many hours without loss of efficiency. The most effective periods of current reversal fall generally between 2 and 10 minutes; usually the greater is the field strength imparted, the higher is the frequency required. The frequency of the commercial alternating current is too high for the inertia

of the system, so that a direct current is employed with mechanical means for reversing it.

The influences of field strength, initial latex concentration and current reversal are shown by the results of typical experiments using an apparatus similar to that shown diagrammatically in Figure 1. This consists of three cells A, B and C, which are separated by cellophane membranes, D. The outer cells contain noncorroding electrodes and are filled with dilute ammonia solutions. The latex to be separated is contained in the middle cell, B. On passage of a current, a stream of latex concentrate travels up the anode membrane and collectes at the upper part of the cell. The following results were obtained with various latices which each contained 0.5 per cent of ammonia.

	Initial concentration of latex (per cent)	Diameter of membranes (cm.)	Distance between membranes (cm.)	Potential gradient (volt per cm.)	Results
Experiment 1					
High concentration (by centrifuging and potential	60	15	4	5	Heavy deposit on anode membrane after 10 min. No stratification
Experiment 2					
Medium concentration and potential	30	15	4	0.75	Stratification after 5 hours plus appreciable deposit on anode membrane
Experiment 3					
Low concentration and potential	5	17	2	0.3	Complete separation of latex after 17 hours, with clear lower serum layer. No deposit on membrane
Experiment 4					
Medium concentration and potential, plus current reversal for few sec. every 4 min.	30	15	4	0.8	Stratification after 5 hours. Concentration of layer 50 per cent. No deposit on membranes

Several modifications of the laboratory apparatus described above were, of course, necessary before the process could be used for the concentration of latex on a production basis.

The figures in the table show, for instance, that the rate of separation at the diaphragm surface is relatively slow, even when current reversal is employed. With only one pair of membranes, the separation must continue until the dispersed particles have migrated throughout the bulk of the latex to the appropriate membrane wall.

It was soon noted that the speed of separation could be increased by introducing a number of diaphragms between the electrode compartments[3], when the layering effect was found to occur simultaneously at each membrane surface without substantially increasing the current consumption. In this way the active membrane surface was very considerably enlarged, with consequent increase in the rate of concentration. In practice, as many as 150 membranes may be used in one electrodecanting unit.

The next step was to avoid interruption of the process when it became necessary to decant off the layers of cream and serum. Experiments showed that if the layers were continuously led away and the volume in the cell was maintained by continuous introduction of fresh latex, separation could proceed

for several days without interruption[4]. Continuous removal of the concentrate also has the advantage that greater uniformity is obtained in the physical condition of the cream, since the time it is subjected to the influence of the electrical potential is considerably reduced.

The input rate must, of course, be controlled to prevent undue turbulence of the main volume of latex in the cell, and careful adjustment of the relative rates of outflow of the concentrate and serum layers is necessary. Experimentation has shown that the best position for introducing the latex is through apertures in the side-walls of the latex vessel situated at about one-third the height of the membrane from the base.

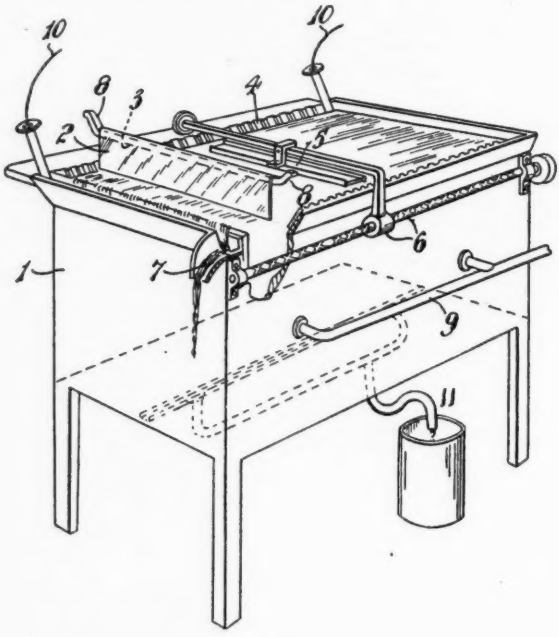

FIG. 2.

In production units the total volume of latex in the separating compartment may be as great as 100 gallons, so that more easily workable nonconducting materials than glass are required. Earlier constructions consisted essentially of a rectangular ebonite tank fitted with a draining channel in the base for removal of the serum, and inlet apertures along the side-walls connected to feed tubes. Each electrode compartment consisted of a thin ebonite box, one wall of which was of cellophane sheet, held in position by an ebonite frame. These boxes, which contained stainless steel electrodes, were placed at each end of the main tank. The vents of the electrode compartments passed through a conically-domed lid clamped to the top of the tank. An outlet was placed at the apex of the dome through which the accumulating upper layer of concentrate was removed. The cellophane membranes were mounted on ebonite frames, which were held in position by slots in the tank walls.

Tanks made of wax-impregnated wood are now alternatively employed, and the domed lid can be replaced by a light dust cover. In this case the

cream rises above the tops of the membranes, and is drained away through tubes at the upper ends of the tank[5]. Figure 2 shows diagrammatically a unit of this type.

The tank (1) contains the diaphragms spaced 1 cm. apart, one of which (2), ir raised from its position where it is held by the support member (3), in slots (4), along the sloping edge of the tank. The diaphragms are of thin cellophane, suspended from the supports and weighted to keep them vertical by glass rods or other suitable material, placed in hems at their lower edges. The electrode boxes (10), are completely immersed in the latex at the ends of the tank with the exception of the electrode gas vent tubes through which the current leads pass. The upper level of the latex may be an inch or more above the tops of the membranes, and the accumulating cream is conducted over weirs (7) at the ends of the tank by the skimming member (5), which passes slowly backwards and forwards in the cream layer. A stream of latex, controlled by a constant head device, is fed by pipes (9) into horizontal channels in the side-walls, and the rate of flow of the serum through (11) is controlled by an adjustable restriction. The method of suspending the diaphragms by the lugs (8) enables them to be removed individually without interrupting the process, should there be eventually any static accumulation of cream in the spaces between the membranes.

There are a number of alternative methods of supporting the membranes in position[6], but in each case it is essential to make the upper supporting member as thin as possible in order to minimize obstruction to the upward flow of cream. All the materials used must, of course, be electrically non-conducting, such as laminated Bakelite or insulated metal strip.

Table 2 gives the results of a typical experimental run carried out by F. J. Paton, using freshly ammoniated latex. A comparatively small unit was

TABLE 2

Hours run	Output per hour in kg.			Per cent total solids		Current strength	
	Cream	Serum	Total	Cream	Serum	Volt	Amperes
1	9.0	10.0	19.0	52.6	11.0	3.0	7.0
4	9.0	10.0	19.0	59.2	8.3	3.0	8.8
10	8.9	10.0	18.9	61.8	7.3	3.1	10.5
50	10.4	10.0	20.4	62.0	5.1	3.0	13.0
100	9.2	10.0	19.2	60.1	6.6	3.0	12.5

Average dry rubber content of latex (0.5 per cent NH_3) = 30 per cent
" " " " " cream = 59.7 " "
" " " " " serum = 1.5 " "

employed, which resembled in principle the one just described. The effective membrane surface was approximately 100 sq. ft. in area, and the output of concentrate averaged a little more than 2 gallons per hour. Larger units may have an output of more than 7 gallons per hour. In practice, several such units may be arranged in batteries, all fed from the same controlled latex supply, with a common current reversal system.

The results indicate the high efficiency of separation obtainable. Under production conditions the loss of rubber in the serum rarely exceeds 1 per cent, which represents a distinct advantage over the efficiency of separation given by the centrifuging method of concentration, where the proportion of rubber in the skin may be as high as 7 per cent. The low loss is of particular importance in the manufacture of highly purified latices for wire insulation and other purposes, where it is necessary to dilute and recream the concentrate, some-

times more than once. The degree of separation also compares favorably with that obtained by the action of creaming agents on latex, with the advantage that there is no trace of creaming agent remaining in the concentrate.

Loss of output caused by stoppages for cleaning purposes is much less with the electrodecantation process than with centrifugal separation, since the periods between cleaning operations are very much longer.

It has been found that the properties of concentrated latices prepared by the two methods are closely similar, as illustrated by the following results of tests on typical samples.

	Once centrifuged latex	Once electrocreamed latex	Twice centrifuged latex	Twice electrocreamed latex
Alkalinity (per cent NH_3)	0.63	0.59	0.67	0.66
Total solids (per cent)	61.3	61.4	61.7	61.8
Dry rubber content (per cent)	59.7	59.8	61.5	61.5
Ash (per cent)	0.45	0.40	0.14	0.14
Nitrogen (per cent)	—	—	0.22	0.23
Color of latex	Grade 1	Grade 1	Grade 1	Grade 1
Color of film (Lovibond units)				
Unaged	1.5	1.0	1.0	<1.0
Aged 16 hours at 95° C	2.5	2.5	1.25	1.5
Z.O.T. stability	64	63	14	15

The color and Z.O.T. stability tests to zinc oxide are similar to those described by Murphy[7].

Observation of the behavior of the two concentrates when used in the manufacture of a wide range of latex products has shown them to be completely interchangeable. The electrodecantation method of concentration shares with the centrifuging process the advantage that there is little tendency for further separation in the latex during prolonged storage, which is not always the case with concentrates prepared by the action of creaming agents.

Experience has indicated that there are a number of factors which influence the rate and general efficiency of concentration by the electrodecantation process. The effects of current density in relation to initial concentration have already been mentioned, but control of temperature, the magnitude of the charge on the particle and the nature of the adsorbed layer of nonrubber components on the surface of the particle are also of importance.

The electrical conductivity increases with rising temperature, causing unnecessary consumption of electricity and a tendency for deposition of cream on the membranes. The heat generated by the passage of the current through the unit also tends to cause a slow rise in temperature as the run proceeds and it is, therefore, often desirable to precool the ingoing latex if the initial atmospheric temperature is high.

The migration velocity of the particles is, of course, dependent on the magnitude of the charge on its surface; if the dispersion is near the isoelectric point very little separation takes place. It is, therefore, sometimes advantageous to increase the charge as far as other conditions will permit to obtain a high rate of separation with low current consumption[8]. In the case of rubber latex, increasing the ammonia content improves the rate of separation in this manner. Polar substances which are also emulsifying agents have similar effects, probably due to their association with the adsorbed surface layer of the particle, thereby increasing its surface charge. Examples of such substances are lipides, cholesterols, salts of cholic and choleic acids and some of the textile wetting agents. Stamberger[9] has proposed for this purpose the use of long-

chain compounds containing hydrophilic groups such as ammonium sorbital borate. Self-emulsifying substances such as diglycol stearate, sorbitol monostearate, etc., in which part of the molecule undergoes ionic dissociation and the remainder contains free groups having an affinity for water, are also claimed to be particularly active in aiding separation.

The charge on the particles in dispersions of some synthetic rubbers is frequently very low, and poor separation is obtained without the addition of substances capable of increasing the charge. For example, very little separation occurred in an aqueous dispersion of Neoprene of 25 per cent concentration with a current density of 1.6 volt per cm. Good layer formation was, however, obtained after the addition of 0.3 per cent of Emulphor O to the dispersion, in this case with the concentrate lowermost, because of the relatively high density of the dispersed particles.

It is well known that, by choosing the nature of the substance added to the latex, it is possible to reverse the charge on the particles. Alkaline positively-charged latices, prepared for instance by the addition of cationic soaps, can be concentrated by the electrodecantation process, the upward flow of cream taking place at the cathode membrane surface. Similar effects are obtained with positively charged acid latices.

Apart from the influence of the charge on the adsorbed surface of the particle, the nature of the surface itself may have an influence on the concentration of the cream layer. If, for instance, the concentration of material at the surface of the particles is considerable and is too strongly hydrophilic in character, the viscosity of the cream for any given concentration is relatively high. In other words, there is only loose packing of the particles in the concentrate layer, and the maximum concentration obtained is correspondingly low. Similar conditions also apply in varying degree to the concentration of dispersions by centrifuging and by the action of creaming agents, both of which rely on gravitational effects. A particular example is found in the purification and concentration of some artificial dispersions of natural rubber where the proportion of hydrophilic colloid required for the inversion is often considerable. In such cases the degree of concentration of the cream is appreciably lower than that obtained in the separation of natural latex.

In conclusion, the author wishes to thank the Dunlop Rubber Company and Dunlop Malayan Estates, Ltd., for permission to publish this paper.

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THE PHOSPHATIDES OF HEVEA BRASILIENSIS *

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The presence of phosphatide in *Hevea* latex had long been suspected, but it was not until 1931 that Rhodes and Bishop[1] isolated phosphatidic material containing 0.59 per cent nitrogen and 1.72 per cent phosphorus from the serum of latex which had been coagulated with ethanol. The crude material of these authors represented 0.2 per cent of the latex and, on treatment with acetone, yielded an insoluble fraction containing 0.88 per cent nitrogen and 2.56 per cent phosphorus (40 per cent of the former product). This latter fraction was, according to the accepted analytical composition of phosphatide, still very impure. The work of Rhodes and Bishop was repeated by Altman and Kraay[2], who isolated in very small amounts a product which gave much the same analyses, and extended the findings of Rhodes and Bishop by showing that the crude phosphatide contained both choline and glycerophosphoric acid.

It is very probable that the phosphatide, although present in such small amount, is one of the important nonrubber components of latex. Judging from the ease with which phosphatides emulsify in aqueous media, there seems little doubt that the phosphatidic material assists in the maintenance of latex as a stable emulsion. It has been suggested by Bollman[3] that crude phosphatide preparations act as natural antioxidants in vegetable oils. This suggestion has been disputed by Diemair and Fox[4] and other workers, who state that this property is not possessed by pure phosphatide, although the complex system from which the phosphatide had been separated was an active antioxidant. Diemair, Strohecker and Reuland[5] have advanced the opinion that the active antioxidant is a protein-phosphatide complex.

The present work was undertaken as part of an investigation of the nonrubber components of latex. The crude phosphatide was prepared by the method of Rhodes and Bishop[1], the preliminary treatment being carried out at the Rubber Research Laboratories, Ceylon, under the direction of Mr. O'Brien, to whom the author's thanks are due. The raw material was treated by the method outlined below. The crude phosphatide was fractionated by a method which was essentially that used by Channon and Foster[6] in their work on the phosphatides of wheat germ. The fractionation resulted in the isolation of a fairly pure form of phosphatidic acid (the possible source of which is discussed later) and an impure form of lecithin. The lecithin fraction contained little or no kephalin (only about 5.5 per cent of the nitrogen in this fraction was amino-nitrogen), a finding which was unexpected.

EXPERIMENTAL

PREPARATION OF THE CRUDE MATERIAL

Freshly tapped latex was coagulated by pouring into 3 volumes of 95 per cent ethanol. The serum was concentrated *in vacuo* at 40°, and the concentrate sealed *in vacuo* and shipped to England. Three samples representing 19.5 liters of latex were received in good condition. The residues were mixed

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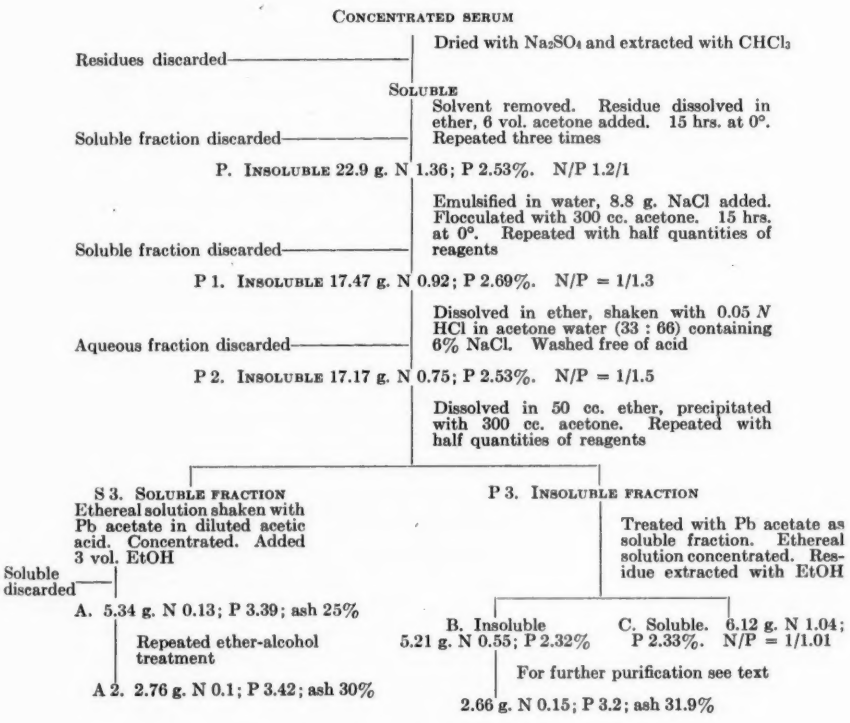
with anhydrous sodium sulfate and extracted with chloroform. The extract was concentrated *in vacuo*, dissolved in ether and the phosphatide precipitated by the addition of 6 volumes of acetone. After 15 hours at 0°, the supernatant liquid was decanted and the residue again treated with ether and acetone. This precipitation was repeated three times. 22.95 grams of material containing 1.36 per cent nitrogen and 2.53 per cent phosphorus were isolated.

Fractionation of the Phosphatide

Plant phosphatides have been shown by several workers[7] to contain lecithin and kephalin, with varying amounts of phosphatidic acid, the latter compound being present as a salt of calcium, magnesium or potassium (some workers state that the sodium salt exists in the plant). It was considered likely that the phosphatide of *Hevea* might be a similar mixture, and for this reason the fractionation procedure was essentially that of Channon and Foster[6]. These workers have described the method in great detail, and the accompanying diagram will suffice to illustrate the course of the fractionation.

Diagram 1


Concentrated serum
Dried with Na_2SO_4 and extracted with $CHCl_3$
Residues discarded
Soluble
Solvent removed. Residue dissolved in ether, 6 vol. acetone added. 15 hrs. at 0°. Repeated three times
Soluble fraction discarded
P. Insoluble 22.9 g. N 1.36; P 2.53%. N/P 1.2/1
Emulsified in water, 8.8 g. NaCl added. Flocculated with 300 cc. acetone. 15 hrs. at 0°. Repeated with half quantities of reagents
Soluble fraction discarded
P 1. Insoluble 17.47 g. N 0.92; P 2.69%. N/P = 1/1.3
Dissolved in ether, shaken with 0.05 N HCl in acetone water (33 : 66) containing 6% NaCl. Washed free of acid
Aqueous fraction discarded
P 2. Insoluble 17.17 g. N 0.75; P 2.53%. N/P = 1/1.5
Dissolved in 50 cc. ether, precipitated with 300 cc. acetone. Repeated with half quantities of reagents
S 3. Soluble fraction
Ethereal solution shaken with Pb acetate in diluted acetic acid. Concentrated. Added 3 vol. EtOH
Soluble discarded
A. 5.34 g. N 0.13; P 3.39; ash 25%
Repeated ether-alcohol treatment
A 2. 2.76 g. N 0.1; P 3.42; ash 30%
P 3. Insoluble fraction
Treated with Pb acetate as soluble fraction. Ethereal solution concentrated. Residue extracted with EtOH
B. Insoluble 5.21 g. N 0.55; P 2.32%
C. Soluble. 6.12 g. N 1.04; P 2.33%. N/P = 1/1.01
For further purification see text
2.66 g. N 0.15; P 3.2; ash 31.9%

Results

Fraction A 2.—This represents a reasonably pure form of lead phosphatidate. Microanalysis gave C 50.6; H 8.3; P 3.42; ash 30.0 (Smith and Chibnall[8] give C 51.2; H 7.7; P 3.48; ash 33 for lead phosphatidate, but the analysis obviously depends on the nature of the fatty acids present). On hydrolysis

it yielded 60.4 per cent fatty acids (I value 112; mol. wt. 290.5). A Twitchell lead soap separation of the latter indicated the presence of 21.6 per cent saturated acids (mol. wt. 280) and 79.4 per cent liquid acids (I value 139; mol. wt. 303). Dihydroxystearic acid, m.p. 130°, and tetrahydroxystearic acid, m.p. 156–157°, were obtained on oxidation of the unsaturated fraction by the method of Haworth[9].

Fraction B.—When isolated, this fraction contained 0.55 per cent nitrogen and 2.35 per cent phosphorus. Extraction with alcohol, or precipitation with alcohol from ethereal solution, did not increase the purity of the fraction; lead was therefore removed and the free acid emulsified in water, precipitated with acetone and the lead salt regenerated. Severe loss occurred during this procedure but 2.66 grams of material were isolated which contained 0.15 per cent nitrogen, 3.15 per cent phosphorus, 31.9 per cent ash, 49.15 per cent carbon, and 7.4 per cent hydrogen. On hydrolysis it yielded 60 per cent of fatty acids (I value 90; mol. wt. 326) of which acids 26 per cent were solid acids (mol. wt. 326) and 74 per cent liquid acids (I value 123; mol. wt. 327). It thus represented a further amount of fairly pure lead phosphatidate. It differed in fatty acid composition from A 2.

Fraction C.—This fraction is a crude lecithin, and it was impossible to effect any further purification. The difficulties of purifying small samples of phosphatide have been stressed by Smith and Chibnall[8] and by Jordan and Chibnall[10]. More recently Diemair, Bleyer and Schmidt[11] have isolated phosphatides from oats, barley and wheat which contained only 1.0 per cent nitrogen and 2.2 per cent phosphorus, although they were apparently free from sugar. Working and Andrews[12] state "It is difficult to imagine what impurities might cling so firmly as not to be removed by the methods used successfully with materials of animal origin". The results obtained by Rhodes and Bishop[1] and by Altman and Kraay[2] indicate that they too found difficulty in purifying their products beyond the limits of 1 per cent nitrogen and 2.5 per cent phosphorus.

Analysis of fraction C.—3.89 grams were hydrolyzed with *N* sulfuric acid for 8 hours. 2.40 grams of fatty acids were recovered (62 per cent yield), I value 111; mol. wt. 315. 2.01 grams were fractionated (Twitchell) into 25 per cent saturated acids (mol. wt. 310) and 75 per cent unsaturated acids (I value 150; mol. wt. 326). Dihydroxystearic (m.p. 125°) and tetrahydroxystearic acid (m.p. 158°) were obtained by oxidation of the unsaturated fraction.

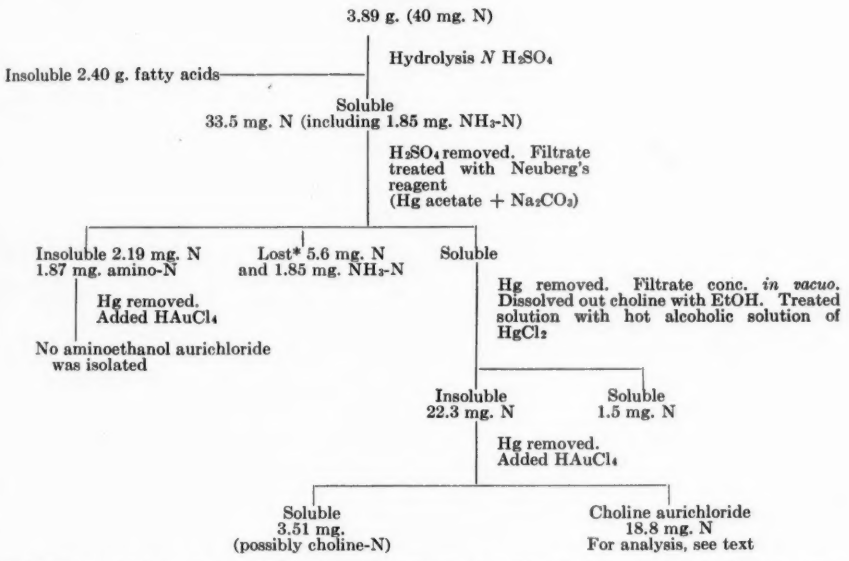
The aqueous fraction was concentrated *in vacuo* and analyzed for bases and reducing sugar. Reducing sugar was determined by the method of Maclean[19] and some 3.3 per cent was found (calculated as glucose). This figure is a minimal one, since appreciable quantities of carbohydrate are decomposed during the acid hydrolysis[8]. Even if this is so, a large proportion of the impurity remains uncharacterized[11]. The total nitrogen of the aqueous fraction was 33.5 mg., some 6.5 mg. (16 per cent) being lost during hydrolysis. Similar losses (22 per cent) were reported by Smith and Chibnall[8] and by Jordan and Chibnall[10], who found that only 65 per cent of the original nitrogen passed into the aqueous filtrate. It is possible that the loss of nitrogen is coupled with the lower amount of reducing sugar (q.v.) in the formation of an insoluble humin. Amino-nitrogen as determined by the method of Van Slyke amounted to approximately 1.85 mg., which, if it were all aminoethanol-nitrogen, would correspond to 8.15 mg. aminoethanol or to about 98 mg. kephalin. (Thus the kephalin content of the fraction cannot be more than

2.5 per cent of the crude phosphatide or about 4 per cent of the calculated phosphatide.)

Isolation of the bases.—The aqueous filtrate was freed from sulfuric acid and analyzed for bases. The method has been described in detail by Smith and Chibnall[8] and depends on the precipitation of primary amines (including amino acids) by the reagent of Neuberg and Kerb[13]. Choline is soluble in the reagent, but is precipitated almost quantitatively by mercuric chloride. The following scheme indicates the course of the separation and the distribution of nitrogen.

The choline aurichloride was isolated in two crops: (1) m.p. 268–270°; Au 44.14; C 13.65; H 3.2; (2) m.p. 265°; Au 44.5; C 13.6; H 3.2. (The analysis in crop 2 was corrected for a small amount of free gold which was found to be contaminating the sample.) $C_5H_{14}ON \cdot AuCl_4$ has m.p. 269–270°, and requires Au 44.5; C 13.5; H 3.2 per cent

DIAGRAM 2


3.89 g. (40 mg. N)
Hydrolysis N H2SO4
Insoluble 2.40 g. fatty acids
Soluble
33.5 mg. N (including 1.85 mg. NH3-N)
H2SO4 removed. Filtrate treated with Neuberg's reagent (Hg acetate + Na2CO3)
Insoluble 2.19 mg. N
1.87 mg. amino-N
Lost* 5.6 mg. N and 1.85 mg. NH3-N
Soluble
Hg removed. Added HAuCl4
No aminoethanol aurichloride was isolated
Hg removed. Filtrate conc. in vacuo. Dissolved out choline with EtOH. Treated solution with hot alcoholic solution of HgCl2
Insoluble 22.3 mg. N
Soluble 1.5 mg. N
Hg removed. Added HAuCl4
Soluble 3.51 mg. (possibly choline-N)
Choline aurichloride 18.8 mg. N For analysis, see text

* The loss of 5.6 mg. N was due largely to the difficulty of washing the large precipitates of HgS. The 1.85 mg. ammonia-N would also be lost during the concentration of the alkaline Neuberg filtrate.

DISCUSSION

From 19.5 liters of latex 22.9 grams of crude material (N 1.36; P 2.53) were isolated. This material, on treatment with water and acetone, yielded 17.5 grams (N 0.92; P 2.69), which is regarded as the true starting material. It represents 0.09 per cent of the latex. From this material were isolated 6.12 grams of lecithin (N 1.04; P 2.33) and 5.42 grams of lead phosphatidate (P 3.2–3.4; ash 30–32; N approx. 0.1). The yield of crude lecithin (60–65 per cent pure) is approximately 35 per cent of the initial material, *i.e.*, 0.03 per cent latex, and the yield of phosphatidic acid is equivalent to 24 per cent of the starting material, *i.e.*, 0.02 per cent latex. The loss of lead phosphatidate was large during the final stages of purification, and the amount of phosphatidic acid might well be about 6.0 grams (35 per cent of fraction P 1).

As stated above, the lecithin fraction was found to contain little or no kephalin. This result was surprising, and it seemed possible that at least some of the phosphatidic acid might be a secondary product derived from the breakdown of kephalin during the concentration of the alcoholic serum.

Although some of the phosphatidic acid may be derived from kephalin breakdown the presence of phosphatidic material in other plants (*Brassicae, Graminae, Leguminosae*, etc.) suggests that one might expect to find the acid as a natural component of fresh latex.

Evidence has been obtained which suggests that phosphatidic acid does occur in fresh latex. Thus the calcium content of P 1 was 0.51 per cent and that of P 2 about 0.1 per cent. (Neither fraction contained magnesium.) The calcium content of P 1, if all the phosphatidic acid isolated (4.2 grams) were present as the calcium salt, would be about 1.2 per cent, and that of P 2 should be negligible. The calcium found suggests that 40 per cent of the phosphatidic acid in P 1 is present as calcium phosphatidate. If any free phosphatidic acid were present in the crude phosphatide (P), one might expect to lose a good deal of it during the ether-acetone fractionation, and the presence of phosphatidic acid after this stage of the fractionation suggests that it is present in salt form in P 1. Unfortunately it was not possible to analyze P 1 for the alkali metals (sodium and potassium) since sodium chloride had been used to assist in the flocculation of P 1 with acetone. To check this point, and the apparent absence of kephalin, a sample of phosphatide was prepared from dried latex (a product in which the breakdown should have been small).

1.48 grams of crude phosphatide were obtained (N 1.2 per cent, P 2.2 per cent) from 850 grams of dried latex. The crude material, after three precipitations with acetone, was dissolved in ether and the solution shaken with 0.05 *N* HCl in 40 per cent acetone-water. The aqueous extract was analyzed for sodium, potassium, calcium and magnesium. Sodium and magnesium were absent. The extract was found to contain the equivalent of 0.48 per cent calcium (estimated by the method of Wiley[14]) and 2.6 per cent potassium (estimated by the method of Hamid[15]).

If these elements were in combination with phosphatidic acid, the crude phosphatide would contain 0.14 gram (9.4 per cent) calcium phosphatidate and 0.41 gram (27.6 per cent) dipotassium phosphatidate. Thus fraction P 1 (diagram 1) should contain 5.9 grams phosphatidic acid (0.03 per cent latex). Only 4.2 grams (0.02 per cent latex) were isolated, since severe losses occurred during the final purification of the phosphatidic acid fractions A 2 and B. It is considered, therefore, that the total amount of phosphatidic acid present in fraction P 1 may well be 5.9 grams (0.03 per cent latex), and that it is probably present as both the calcium and potassium salts in the ratio of 1 : 3.

No amino-nitrogen, in amounts greater than those suggested above, could be detected in the phosphatide, and it must be concluded that the phosphatide of *Hevea Brasiliensis* does not contain appreciable amounts of kephalin. This finding is in keeping with that of Altman and Kraay[2].

The fatty acids of the fractions A, B and C had an iodine value of 90–112 and contained 21–26 per cent of saturated acids; the fatty acids from the glycerides[16] had an iodine value of 135–148, and contained 24–26 per cent saturated acids. Thus the glyceride fatty acids are slightly more unsaturated than the phosphatide fatty acids. This finding is similar to those of Smith and Chibnall[17], who found that the glyceride and phosphatide fatty acids of cocksfoot grass (*Dactylis glomerata*) had iodine values of 170 and 128–144, respectively.

In a recent paper, Baker[18] stated that, on purifying latex by creaming or centrifuging, the nitrogen content of the rubber was reduced to a lower limit of 0.03 per cent. This nitrogen was said to be due to the "phospholipin-sterol complex which is also thought to be associated with the rubber phase". Now if the pure phosphatide of *Hevea Brasiliensis* is assumed to be only lecithin, the residual nitrogen referred to by Baker corresponds to the presence in the crude rubber of 1.7 per cent of lecithin. If there is any phosphatidic acid present, the amount of phosphatide would be even higher (1.7–3.4 per cent). Now the maximum amount of phosphatide (even in the crude condition) which has been isolated is 0.2 per cent (N 0.59; P 1.72)[1] and there is every reason to suppose that some of the nitrogen in this product is nonphosphatide nitrogen. The assumption of Baker could be tested by a determination of the phosphorus content (0.06 if the phosphatide is only lecithin). The statement of Baker infers that the phosphatide is removed from the rubber globule only with great difficulty. It must be pointed out, however, that the lipin was isolated from the serum after coagulation of the latex with alcohol. The fact that crepe rubber contains little or no phosphatide may indicate that the reverse is the case, namely, that the phosphatide, although assisting in the maintenance of the latex in equilibrium, will appear in the aqueous fraction when that equilibrium is upset.

ACKNOWLEDGMENT

The author wishes to express his thanks to W. T. Chambers for kindly carrying out the carbon and hydrogen analyses for him, and to Prof. A. C. Chibnall for much helpful criticism and advice.

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AN ELECTROPHORETIC STUDY OF THE PROTEINS IN RUBBER LATEX SERUM *

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The proteins in rubber (*Hevea brasiliensis*) latex serum have been the subject of several researches during the past fifteen years. Some of this work has been concerned with the chemical properties of the proteins[1] and some with their electrophoretic properties[2]. Recently, the improvements introduced by Tiselius[3] in electrophoretic technique have made it possible to increase the precision and significance of electrophoretic measurements very considerably. The work here reported is part of a program of electrophoretic research on latex proteins. This program was initiated in an attempt to obtain information which would be helpful in correlating protein behavior with the colloidal and other properties of latex.

EXPERIMENTAL

The electrophoresis apparatus.—The apparatus was supplied by the Klett Manufacturing Company of New York City, and was built according to specifications furnished by L. G. Longsworth of the Rockefeller Institute in New York. Details may be found in Longsworth's publications[4]. A few modifications of the apparatus are described in the following paragraphs.

Illumination system.—Many latex-serum samples used in this work did not transmit the visible lines of the mercury spectrum very well. In some cases this was on account of slight turbidity, in others on account of color. The transmission coefficient of such solutions was found to be much greater in the red. Consequently, the mercury arc supplied with the apparatus was replaced by a 500-watt Tungsten filament projection lamp, in conjunction with a Corning no. 246 lighthouse red filter. The object of this arrangement was to produce the most uniform possible exposure of photographic plate over the entire length of the cell image when the cell contained either a turbid or colored protein solution separated from a colorless buffer solution by a boundary in the exposed part of the cell. This expedient did not in all cases yield perfect results, but it was much more generally practicable than the use of the mercury arc, and well-defined Schlieren patterns were obtained[5]. Wratten and Wainwright Contrast Thin Coated Panchromatic plates were used. They are insensitive at wave lengths greater than 6800 Å., and the red filter cuts out all light of wave length less than 5600 Å. These figures are extreme values. The range of practical intensities lies between 5800 and 6600 Å.

In using the mercury arc in cases where this was feasible, it was found advantageous to introduce a Corning yellow-yellow filter to filter out the violet part of the mercury spectrum. This resulted in the production of straighter base lines in the Schlieren diagrams by the elimination of a small dispersion effect due to some undetermined cause in the optical system.

Electrodes and source of potential.—The silver-silver chloride electrodes were replaced by copper electrodes dipping into a concentrated copper sulfate solu-

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tion. These electrodes are perfectly reversible and are easier to prepare than the silver-silver chloride system. In addition, they require no special care or attention after they are made. The authors used no. 14 copper wire wound into a compact flat coil and soldered to a small copper tube which was cemented to a piece of glass tubing, just as in the case of the silver electrodes. When an alkaline buffer solution was used, a layer of saturated sodium sulfate solution was introduced between the buffer and copper sulfate solutions to prevent the formation of insoluble basic copper compounds at the liquid junction.

The potential difference applied to the electrophoresis cell and electrodes was furnished by a bank of 45-volt heavy-duty B batteries. Conditions were always adjusted to make the power consumption less than three watts in the cell and electrode system.

The field strength within the electrophoresis cell was calculated from measured values of the current passing, the specific conductance of the solution and the cross-section of the cell.

Compensating device for shifting boundaries.—The motor-driven compensating device was replaced by a gravity feed through a one-meter U-shaped length of capillary glass tubing, of 1-mm. inside diameter, which was connected at one end to the closed electrode vessel and at the other end to a separatory funnel which served as a reservoir.

Ammonia-preserved serum from Sumatra normal latex.—This was a one-gallon lot which was prepared on the plantations of the U. S. Rubber Company in Sumatra by freezing fresh unpreserved normal *Hevea* latex. Freezing caused complete coagulation of the rubber into a coherent clot. After thawing, the rubber-free serum was expressed, preserved with 2 per cent ammonia and shipped to America in a stoppered glass container.

Serum from unpreserved Sumatra normal latex.—Fresh unpreserved normal *Hevea* latex was frozen on the plantations in Sumatra and shipped in the frozen state to America. After this material had been thawed, the rubber-free serum was expressed and refrozen as quickly as possible to prevent deterioration. Serum thus prepared and containing no chemical preservative had a light straw color and a perfectly sweet odor. Its *p*H value was 6.4 at 25°. When kept stored in glass in the frozen state at −20° it retained these characteristics over a period of months, with no signs of any deterioration.

Serum from unpreserved normal Florida latex.—This latex (*Hevea*) was treated exactly like that prepared in Sumatra, but it originated in the Plant Introduction Garden of the United States Department of Agriculture, Coconut Grove, Florida. The *p*H value of this serum was also 6.4 at 25°.

Direct preparation of latex serum for electrophoresis.—All electrophoresis determinations were made in solutions which were well buffered to secure adequate *p*H control. Each serum sample was, therefore, dialyzed exhaustively against the appropriate buffer solution at the temperature of the Tiselius thermostat. Conductance measurements were used to determine the extent of dialysis. Conductance and *p*H measurements (glass electrode) were made at the temperature of the cold thermostat which was held at +1°.

Concentration of latex serum proteins.—It was necessary in several cases to have a more concentrated solution of the serum proteins than that in which they naturally occur in serum from frozen latex. For this purpose dry serum solids were prepared by the technique of vacuum sublimation of rubber-free frozen serum. This technique has been used extensively in the past by workers with animal sera[6]. The latex serum solids thus obtained contained some hygroscopic material which could be largely removed by dialysis with distilled

water for twenty-four hours before starting the vacuum sublimation process. Dialysis could not be carried farther than this without causing partial flocculation and denaturation of the proteins. When properly prepared, the dried serum solids showed no outward signs of deterioration, and could be completely redissolved in aqueous solutions at all *p*H values at which the original serum was stable. All concentrated latex protein solutions used in this work were prepared from completely vacuum dried samples. Dialysis against buffer solutions was carried out prior to electrophoresis in the case of these concentrated solutions, just as in the case of the native serum samples.

Buffer solutions.—All buffer solutions were made by use of uni-univalent electrolytes at an ionic strength equal to 0.1. In the following table the acid-base combinations used to cover the various segments of the *p*H interval between 2.0 and 10.5 are listed. *p*H values were measured with the glass

*p*H interval	Acid	Base
2 – 4	HCl	Glycine
4 – 5.5	Acetic	NaOH
5.5– 7	Cacodylic	NaOH
7 – 8.5	HCl	Triethanolamine
9 –10.5	Glycine	NaOH

electrode at 1°. To calibrate the electrode, it was assumed, following Harned and Ehlers[7], that the ionization constant of acetic acid at 0° was $10^{-4.79}$ at an ionic strength of 0.1.

RESULTS AND DISCUSSION

General remarks on the interpretation of Schlieren diagrams.—The detailed theory of the Schlieren scanning method of measuring refractive index gradients has been described elsewhere[8]. It will be recalled that in electrophoretic Schlieren diagrams the position and the time rate of displacement of a given peak along the axis of abscissas give, respectively, a direct index of the position and the rate of motion of the corresponding protein boundary within the cell. From this the electrophoretic mobility may be calculated by the introduction of the appropriate magnification and electric field factors. Each peak corresponds to a separate boundary. The ordinate of a Schlieren diagram is proportional to the gradient of refractive index and, hence, the area under the diagram included between two abscissas is proportional to the total refractive index change between the two abscissas. If the relationship between concentration and refractive index is known, then the area under a Schlieren diagram, by introduction of the proper optical factors, gives a measure of the concentration change of solute from one part of the cell to another.

Protein components of latex serum.—Figure 1 shows electrophoretic Schlieren diagrams (rising boundaries) at three *p*H levels for each of two samples of protein from Sumatra and Florida unpreserved whole-latex serum. The presence of seven resolvable components is evidenced by inspection at the *p*H values of 6.85 and 8.43. Only six components are resolvable at *p*H 10.4, since I and V have the same mobility at this point.

Complete electrophoretic Schlieren diagrams for the proteins in whole-latex serum can be obtained only with concentrated serum, since two of the minor components (VI and VII) are present in such small quantities that they are not detectable at their natural concentrations in serum from frozen latex.

It is not known at present how to classify these electrophoretically resolvable components in terms of usual protein nomenclature. So far as the authors

are aware, the only classification which has ever been made depends on the separation of the whole protein into the so-called glutelin, globulin and albumin fractions[1]. Probably the protein components of unpreserved latex serum can be fitted into this classification, but it will require a combination of analytical results with those of electrophoresis experiments.

Comparison of Florida and Sumatra latex serum proteins.—The Schlieren diagrams of Figure 1 show that the Florida and Sumatra protein samples are

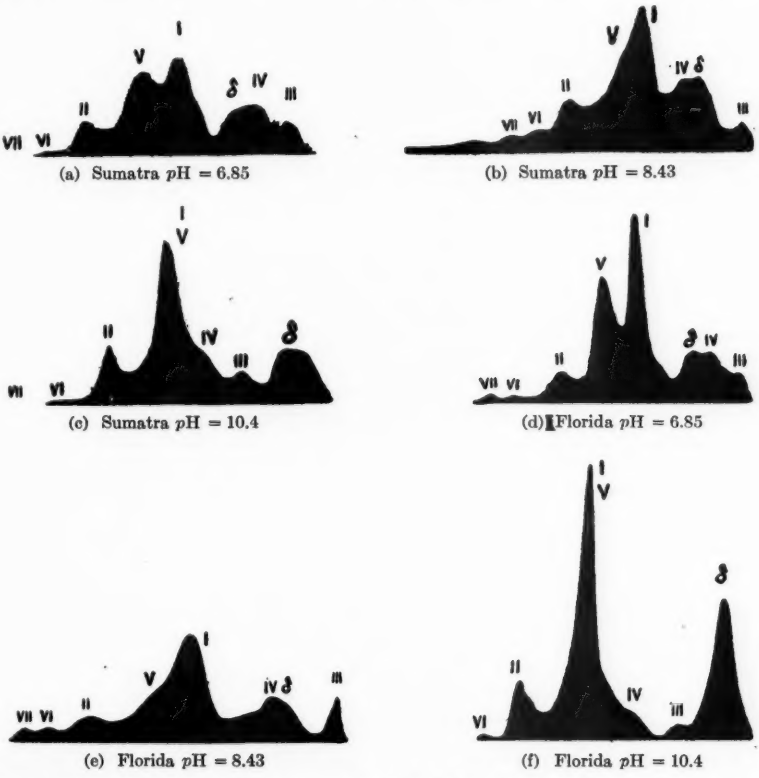

FIG. 1.—Schlieren diagrams showing comparison of Florida and Sumatra latex serum proteins, all samples concentrated 3/1.

electrophoretically very similar in most respects. The number of resolvable components is the same, and the mobilities and relative abundance of the various components are nearly the same. The mobility figures are given in Table I and are represented graphically in Figure 2.

Inspection of the diagrams in Figure 1 shows that the relative abundance is about the same in the sera from the two sources and also that the total protein content is not much different in the two cases. A quantitative comparison of the areas under the Schlieren diagrams is impossible, since through an unfortunate oversight base line photographs were not recorded in all cases. No attempt has been made to fit the correct base lines in any case, since no use is made of them. The principal difference between the Florida and Sumatra diagrams lies in the sharpness of the peaks. The sharper peaks in the

TABLE I

MOBILITY *versus* *p*H VALUES FOR TOTAL SERUM PROTEINS FROM SUMATRA AND FLORIDA LATEX

Component	Mobility in microns per second per volt per cm.					
	*p*H = 6.85		*p*H = 8.43		*p*H = 10.4[a]	
	Sumatra	Florida	Sumatra	Florida	Sumatra	Florida
I	−0.200	−0.210	−0.355	−0.335	−0.575	−0.580
II	− .590	− .615	− .690	− .680	− .880	− .980
III	+ .255	+ .240	+ .120	+ .110	− .230	− .165
IV	+ .090	+ .120	− .150	− .160	Not resolved	
V	− .335	− .360	Not resolved		− .575	− .580
VI	− .800	− .825	− .850	− .825	−1.18	−1.21
VII	− .955	− .915	− .985	− .915	−1.39	−1.53

[a] This *p*H value is actually an average figure. The Sumatra values were measured at *p*H 10.2 and the Florida values at 10.6.

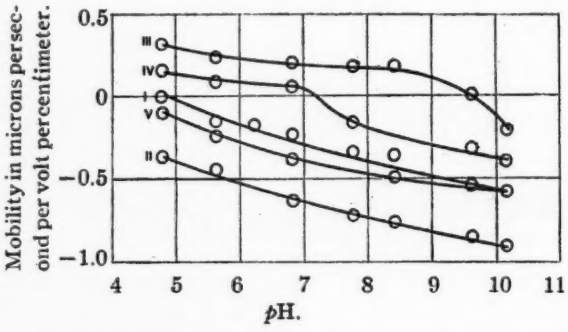

FIG. 2.—Mobility–*p*H curves for five protein components of latex serum.

TABLE II

MOBILITY *versus* *p*H DATA ON SUMATRA LATEX SERUM PROTEINS

*p*H	Component. . I	II	III	IV	V
4.79	0	−0.360	+0.330	+0.160	−0.105
5.66	− .150	− .445	+ .245	+ .089	− .245
6.85	− .230	− .630	+ .200	+ .064	− .385
7.81	− .340	− .735	+ .170	− .170	. . .
8.43	− .365	− .755	+ .177	. . .	− .495
9.67	− .530	− .850	. . .	− .325	− .530
10.18	− .575	− .910	− .212	− .395	− .575

Florida sample indicate a greater degree of electrophoretic homogeneity of the several components in this than in the Sumatra sample. The cause is not definitely known, but the difference probably indicates more sanitary handling and less incipient deterioration before freezing on the Florida experimental plot than on the Sumatra plantation.

The similarity of Schlieren patterns obtained from latex sera with such widely different geographical origins is not surprising. Workers with human sera[9] have found that the Schlieren pattern of normal human serum is nearly independent of the source of the serum, and that only abnormal or pathological conditions cause large departures from the characteristic normal pattern. The results reported here on latex serum proteins are not sufficiently extensive to be accepted as proof that the geographical origin of latex from a healthy tree

has no effect on the Schlieren pattern of the serum proteins, but the close similarity of the patterns here presented, taken together with the findings of investigators in other related fields, makes such an assumption seem plausible. If this is true, it is a matter of some practical interest in latex technology. It would indicate that variations in normal latex from healthy trees cannot be ascribed to qualitative variations in the protein content of the serum before tapping. Variations traceable to the proteins must be due, then, to variations in handling conditions and preservation procedures.

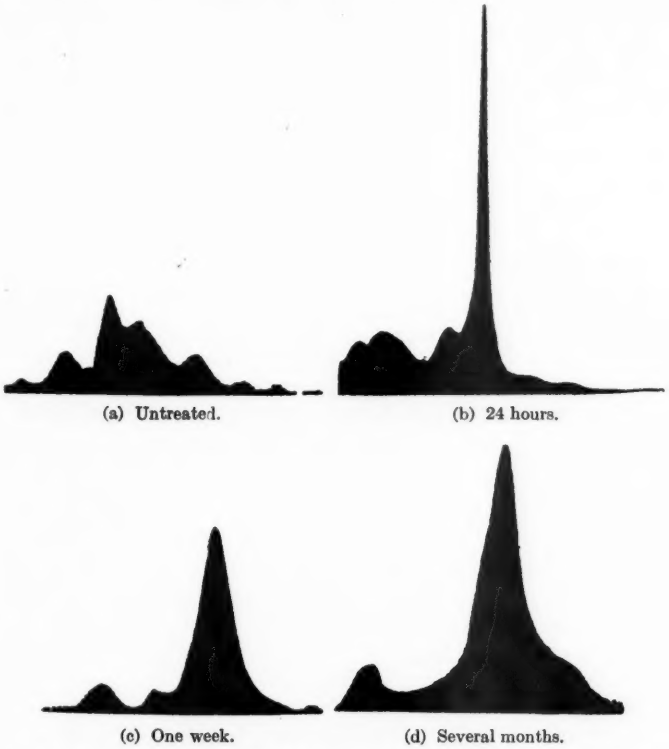

FIG. 3.—Schlieren diagrams showing effects of treatment of latex serum with 1% NH_3 for various lengths of time: (a), (b), (c) concentrated 3/1; (d) concentrated 5/1; *p*H = 6.85.

Relationship between pH and electrophoretic mobility.—Figure 2 shows the mobility-*p*H curves for five of the seven protein components of unpreserved whole latex serum. These curves were plotted from data obtained from the electrophoresis of unconcentrated serum before the discovery of the minor components VI and VII, which were detectable only after concentration. It was found impossible to follow these curves below *p*H 4.79. Some insoluble material was precipitated below *p*H 5.7, but Schlieren diagrams continued to exhibit peaks corresponding in an orderly way to five components down to *p*H 4.79. Below this level it is not possible on the basis of data in hand to correlate the diagrams obtained with the behavior of the proteins above *p*H 4.79.

The wide distribution of isoelectric points on the *p*H scale is a matter of interest. Since two of these isoelectric points occur at *p*H 7.2 and *p*H 9.7, the

persistence of positively charged protein components at high *p*H values is demonstrated. This may be accountable for the known stability of fresh unpreserved latex toward the addition of acid, whereas the negative components stabilize with respect to added alkali.

Effect of ammonia treatment of latex serum.—The progressive effects of free ammonia at high *p*H levels on the proteins from unpreserved latex serum are shown by a comparison of the Schlieren diagrams (falling boundaries at *p*H 6.85) contained in Figure 3. The final effect of ammonia treatment is to reduce the number of resolvable components from seven to two.

Ammonia is of interest because of its commercial importance as a latex preservative. In its effect on latex proteins, the presence of ammonia constitutes an abnormal condition in the serum and would be expected to produce departures from the characteristic normal pattern for untreated latex serum. It has been found that pathological conditions in human sera sometimes cause an abnormal change in the ratios of the various protein components of the sera. Although the detailed nature of the change in latex protein dissolved in ammonia solution is not known, one important observation may be made. The principal component of the exhaustively ammoniated protein solution has a higher numerical value of negative mobility than the principal component of unpreserved latex protein on the alkaline side of the isoelectric point. This is shown in Table III, and probably accounts at least in part for the well-known

TABLE III

MOBILITY VALUES OF PRINCIPAL PROTEIN COMPONENT OF LATEX SERUM AFTER VARIOUS LENGTHS OF TIME IN 1% NH_3 SOLUTION *p*H 6.85

Time in 1% NH_3	Mobility in microns per sec. per volt per cm.
Untreated	−0.210
24 hours	− .332
7 days	− .565
Several months	− .465

rise in mechanical stability of latex within a short time after ammonia preservation is applied on the plantations.

It should be noted that soaps produced by the hydrolysis of resins may also be partially responsible for this increase in stability.

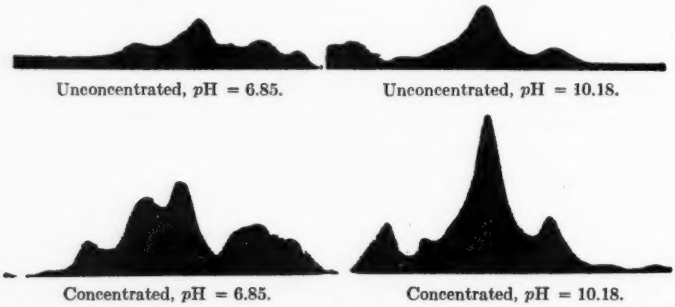

FIG. 4.—Schlieren diagrams showing effects of vacuum sublimation on latex serum proteins.

These experiments were all carried out on vacuum dried protein redissolved at a concentration three times that occurring in serum from frozen latex, except as indicated in Figure 3.

Effects of vacuum sublimation.—Figure 4 shows a comparison of Schlieren diagrams obtained with unconcentrated serum and diagrams obtained with concentrated solutions of vacuum dried serum solids.

The diagrams made in experiments with concentrated protein solutions show more detail than those made with dilute solutions, and tend to confirm the latter. The correspondence of the peaks representing the various components is taken to be an indication that no important change in the electrophoretic properties of the proteins was produced by the sublimation process.

Acknowledgment.—The writers wish to acknowledge their indebtedness to H. F. Loomis, of the United States Department of Agriculture, for his courtesy and coöperation in furnishing the fresh unpreserved latex from Florida. The writers are also indebted to L. G. Longsworth, Dan Moore and E. J. Cohn for helpful discussions of experimental methods.

SUMMARY

1. The serum from unpreserved rubber (*Hevea brasiliensis*) latex contains seven electrophoretically distinct protein components. The proteins from whole serum originating in Sumatra and Florida give very similar results in electrophoresis experiments.

2. The relationship between electrophoretic mobility and *p*H has been determined for five of the seven protein components of unpreserved total latex serum. The results are considerably different from those reported by workers with ammonia-preserved latex, and tend to clarify observed differences in the stability behavior of unpreserved and preserved latex.

3. Ammonia-preservation treatment rapidly alters the electrophoretic behavior of the native protein components of latex serum and reduces the number of resolvable components from seven to two.

4. The preparation of dry latex protein from rubber-free latex serum can be accomplished by the vacuum sublimation of frozen serum. This process does not appear to produce important changes in the electrophoretic properties of the total serum proteins.

5. Minor modifications of the electrodes and of the standard illumination system in the electrophoresis apparatus are described.

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PROPERTIES OF RUBBER SOLUTIONS AND GELS *

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Rubber solutions, like other solutions of long-chain molecules in small-molecule solvents, show large deviations from Raoult's law, even when the heat of mixing is small. As Meyer[1] pointed out, this can be attributed to a large entropy-of-mixing effect, a result of a randomness of orientation of each segment of the solute molecule chain relative to the adjacent segments. This concept has been put on a quantitative basis by the writer[2] and, independently, by Flory[3].

Combining his theoretical equation for the entropy of mixing with an approximate expression, due to van Laar[4], Scatchard[5], and Hildebrand[6], for the heat of mixing, the writer deduced the following equation for the thermodynamic activity of the small-molecule component:

$$\ln a_1 = \ln V_1 + \left(1 - \frac{\overline{V}_1}{\overline{V}_2}\right) V_2 + \mu_1 V_2^2 \qquad (1)$$

where a_1 = thermodynamic activity
V_1, V_2 = volume fractions
$\overline{V}_1$, $\overline{V}_2$ = partial molal volumes of components (for present purpose assumed equal to actual molal volumes, V_1 and V_2 of pure components)
μ_1 = a constant (approximately), characteristic of a given solute-solvent system at a given temperature

The corresponding equation for $\ln a_2$ is like Equation 1, except for the interchange of all subscripts.

Such properties as vapor pressures, osmotic pressures, freezing-point depressions and solubilities are related by simple thermodynamic equations to the activities of the solution components. There are, thus, ample data on a wide variety of systems, available for testing Equation 1. These tests have yielded such uniformly satisfactory results[11] that this equation must represent a close approximation to the truth.

In this paper Equation 1 will be applied to solutions of rubber.

THE "CONSTANT" μ_1

The quantity μ_1 depends in part on the heat of mixing and in part on the departure from perfect randomness of mixing of the molecules in the solution. Crudely speaking, it is a measure of the preference of each molecule (or submolecule) to have other like molecules (or submolecules) rather than units of the other kind, for immediate neighbors.

Rearranging Equation 1:

$$\frac{\ln a_1 - \ln V_1}{V_2} - 1 = -\frac{\overline{V}_1}{\overline{V}_2} + \mu_1 V_2 \qquad (2)$$

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 35, No. 2, pages 216–220, February 1943. This paper was presented before the Division of Rubber Chemistry at the 104th Meeting of the American Chemical Society, Buffalo, N. Y., September 10, 1942.

A plot of the left-hand member of this equation against V_2 should, therefore, give a straight line (if μ_1 is constant) having a slope equal to μ_1 and an intercept at $V_2 = 0$ (*i.e.*, at infinite dilution) equal to $-\overline{V}_1/\overline{V}_2$ (hence, for a given solvent, inversely proportional to the molecular weight of the solute). Any accurate method for determining a_1 as a function of concentration (A_2) will thus serve to give the molecular volume, and so the molecular weight, of the solute particles and also the value of μ_1.

If data are available on osmotic pressure (Π), for example, substitution may be made into Equation 2:

$$\ln a_1 = -\frac{\Pi \overline{V}_1}{RT} \approx -\frac{\Pi V_1}{RT} \tag{3}$$

where R = molal gas law constant
T = absolute temperature

The value of R depends, of course, on the units in which Π and V_1 are expressed. Also, $\ln V_1$ may be expanded:

$$\ln V_1 = \ln (1 - V_2) = -V_2 - \frac{V_2^2}{2} - \frac{V_2^3}{3} - \cdots \tag{4}$$

and if the solution is sufficiently dilute, all but the first two or three terms may be dropped. This leads to the relation:

$$\frac{\Pi}{V_2} - \frac{RT\,V_2^2}{3\,V_1} = \frac{RT}{V_2} + \frac{RT}{V_1}\left(\frac{1}{2} - \mu_1\right) V_2 \tag{5}$$

the second term on the left-hand side usually being negligible. Similar equations involving concentrations in other units are readily deduced. If the concentrations are in grams of solute per cc. of solution (C_2), for example:

$$\frac{\Pi}{C_2} - \frac{RTC_2^2}{3\,V_1 d_2^3} = \frac{RT}{M_2} + \frac{RT}{V_1 d_2^2}\left(\frac{1}{2} - \mu_1\right) C_2 \tag{6}$$

where d_2 = density of pure solute
M_2 = molecular weight of pure solute

If the data at hand are cryoscopic, the equations corresponding to 3, 5, and 6 are:

$$\ln a_1 = -\frac{\Delta H_{f,1} \vartheta_f}{RT_{f,1}^2} \tag{7}$$

$$\frac{\vartheta_f}{V_2} - \frac{RT_{f,1}^2\,V_2^2}{3\,\Delta H_{f,1}} = \frac{RT_{f,1}^2\,V_1}{\Delta H_{f,1}\,V_2} + \frac{RT_{f,1}^2}{\Delta H_{f,1}}\left(\frac{1}{2} - \mu_1\right) V_2 \tag{8}$$

$$\frac{\vartheta_f}{C_2} - \frac{RT_{f,1}^2\,C_2^2}{3\,\Delta H_{f,1} d_2^3} = \frac{RT_{f,1}^2\,V_1}{\Delta H_{f,1}\,M_2} + \frac{RT_{f,1}^2}{\Delta H_{f,1} d_2^2}\left(\frac{1}{2} - \mu_1\right) C_2 \tag{9}$$

where $T_{f,1}$ = freezing point, ° K

$\Delta H_{f,1}$ = molal heat of fusion of solvent

In agreement with Equation 6, graphs of Π/concentration against concentration, for very dilute rubber solutions (as for solutions of other long-chain compounds[13]) show a rectilinear relation[14]. A typical example is shown in Figure 1.

In this case, omission of the second term on the left-hand side of Equation 6 makes little difference. This is not true, however, if the data are for somewhat

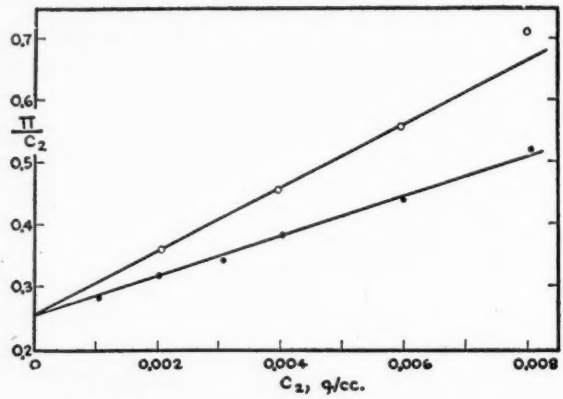

FIG. 1.—Dependence of osmotic pressure on concentration, for gutta-percha solutions in toluene (black circles) and in carbon tetrachloride (open circles).

Data from Staudinger and Fischer[7]. The inclusion of a term ($-RTC_2^2/3V_1d_2^3$) would lower the two right-hand points (at $C_2 \approx 0.008$) about 0.005.

higher concentrations, as illustrated by Figure 2. Over the concentration range shown, the agreement with a straight-line relation is not much altered. (In this case the inclusion of the second term actually results in slightly poorer agreement; more often the agreement is bettered.) There is a significant difference, however, between the intercepts (at $C_2 = 0$) and, hence, between the molecular weights calculated from them.

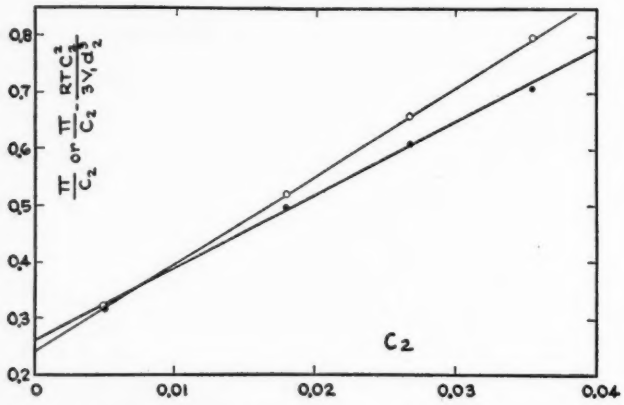

FIG. 2.—Effect of the term $-RTC_2^2/3V_1d_2^3$ on extrapolation of osmotic pressure data to infinite dilution, to obtain molecular weights.

The intercepts give $M_2 = 94{,}000$ with this term and "M_2" = 102,000 without it. Data of Caspari[9] on solutions of "fresh" rubber in light petroleum.

Similar remarks apply to the use of cryoscopic data to obtain molecular weights. As Figure 3 shows, somewhat different molecular weights are deduced, depending on whether or not the second term of Equation 9 is included.

It is obvious from these figures and from Equations 6 and 9 that "molecular weights" computed from the limiting equations:

$$\frac{\Pi}{C_2} = \frac{RT}{M_2} \tag{10}$$

$$\frac{\vartheta_f}{C_2} = \frac{RT_{f,1}^2 V_1}{M_2 \Delta H_{f,1}} \tag{11}$$

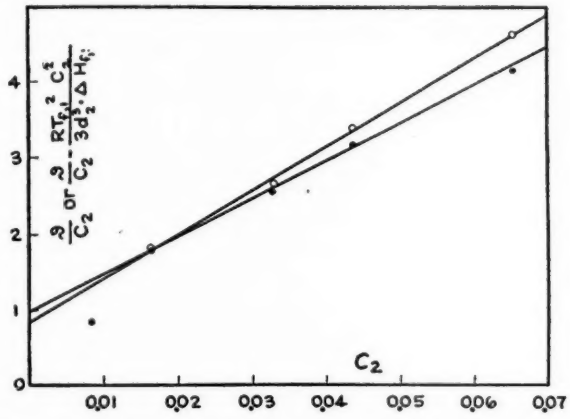

FIG. 3.—Effect of the term $-RT_{f,1}^2C_2^2/3d_2^2\Delta H_{f,1}$ on extrapolation of cryoscopic data to infinite dilution, to obtain molecular weights.

The intercepts give $M_2 = 27{,}000$ with this term and "M_2" = 23,000 without it. Data of Kemp and Peters[8] on solutions of rubber (preparation 2, fraction 2) in cyclohexane. (They give "cryoscopic molecular weights", obtained without extrapolation, ranging from 6050 to 30,870 for this material.)

or other equations equivalent to them, are true molecular weights only if the concentration is not significantly different from zero or if μ_1 for the particular combination of solvent and solute is close to $\frac{1}{2}$. Otherwise the so-called molecular weights are erroneous, and their use is likely to lead to false conclusions[16], as pointed out by Gee[17].

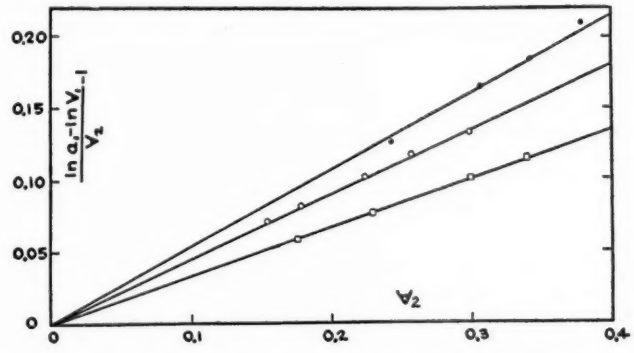

FIG. 4.—Determination of μ_1 from swelling pressure data of Posnjak[10], according to equation 2.
● Rubber-ether, $\mu_1 = 0.55$
○ Rubber-thiophene, $\mu_1 = 0.45$
□ Rubber-cymeme, $\mu_1 = 0.33$

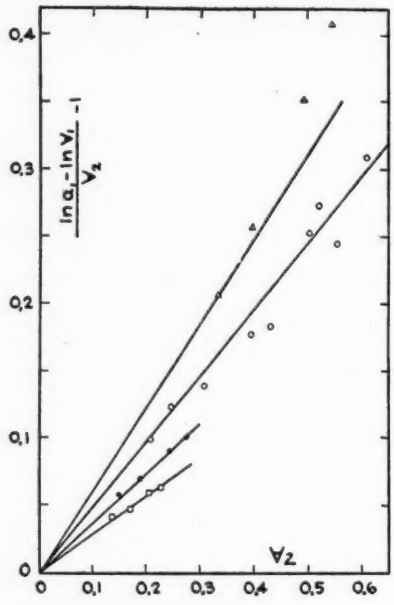

FIG. 5.—Determination of μ_1.
○ Rubber-carbon disulfide, $\mu_1 = 0.49$; vapor pressure data of Stamberger[12].
△ Rubber-ethylene chloride, $\mu_1 = 0.62(?)$; swelling pressure data of Posnjak[10].
● Rubber-chloroform, $\mu_1 = 0.37$; swelling pressure data of Posnjak[10].
□ Rubber-carbon tetrachloride, $\mu_1 = 0.28$; swelling pressure data of Posnjak[10].

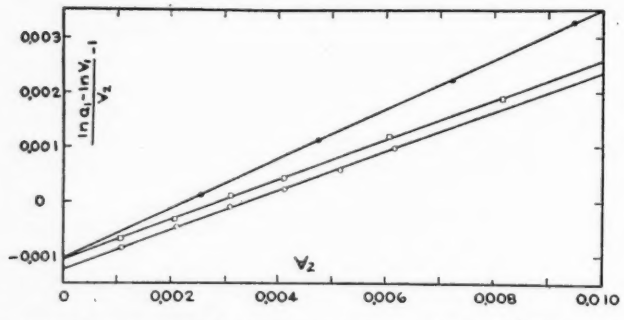

FIG. 6.—Determination of μ_1 and M_2 from osmotic pressure data of Staudinger and Fischer[7] on solutions in toluene.
● Hydrorubber (less soluble fraction), $\mu_1 = 0.45$, $M_2 = 90{,}000$.
□ Gutta-percha (preparation II), $\mu_1 = 0.36$, $M_2 = 98{,}000$.
○ Balata (preparation I), $\mu_1 = 0.36$, $M_2 = 84{,}000$.

Values of the constants μ_1 for different systems can be computed from the slopes of the straight lines obtained when the quantity $(\Pi/C_2) - (RTC_2^2/3V_1d_2^3)$ is plotted against C_2 or from corresponding plots of cryoscopic data. If the data to be used are for more concentrated solutions, however—for example, Posnjak's data[10] on swelling pressures and Stamberger's[12] and Gee and Treloar's[18] on vapor pressure—it is more convenient to compute $\frac{\ln (a_1/V_1)}{V_2} - 1$

and plot this against V_2, as suggested by Equation 2. Figures 4 to 9 are examples. Table I lists values of μ_1, obtained from these and similar graphs, for various systems containing rubber, as well as for a few containing gutta-percha, hydrorubber, etc.

The value of μ_1 is apparently independent of molecular weight, as it is for other high-polymer systems studied. The slight differences in slope shown in Figure 7 are probably due in part to experimental error; on the other hand, minor differences in the chemical nature of the molecules (and so in their attractions for one another and for the solvent, resulting in differences in μ_1) would be expected from the differences in the chemical treatment undergone by the various samples studied.

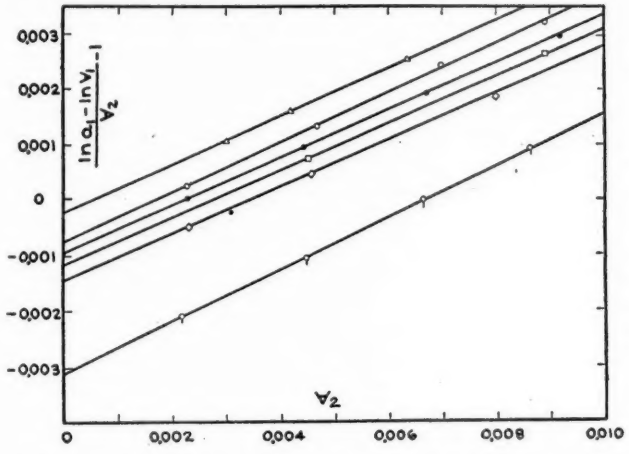

FIG. 7.—Determination of μ_1 and M_2 from osmotic pressure data by Staudinger and Fischer[7] on solutions in toluene.

△ Rubber treated with Al_2O_3, $\mu_1 = 0.44$, $M_2 = 395{,}000$.
○ Masticated rubber (technical; less soluble fraction), $\mu_1 = 0.45$, $M_2 = 130{,}000$.
● Crepe rubber I, oxidized with $KMnO_4$, $\mu_1 = 0.43$, $M_2 = 102{,}000$.
□ Masticated rubber (technical; more soluble fraction), $\mu_1 = 0.43$, $M_2 = 83{,}000$.
◇ Masticated rubber (more soluble fraction), $\mu_1 = 0.42$, $M_2 = 68{,}000$.
♀ Cyclic rubber made with $SnCl_4$, $\mu_1 = 0.46$, $M_2 = 32{,}000$.

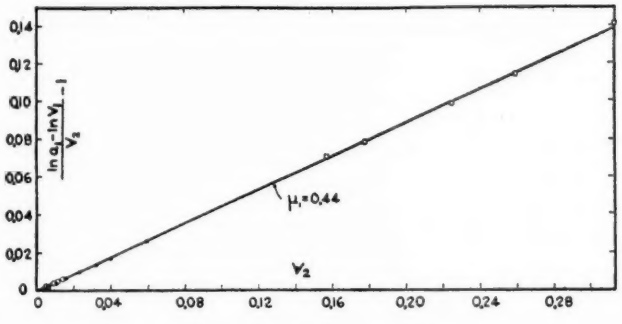

FIG. 8.—Rubber-benzene system.

○ Osmotic pressure data (40° C) of Kroepelin and Brumshagen[15].
● Osmotic pressure data (25° C) of Caspari[9].
□ Swelling pressuredata (15–20° C) of Posnjak[10].

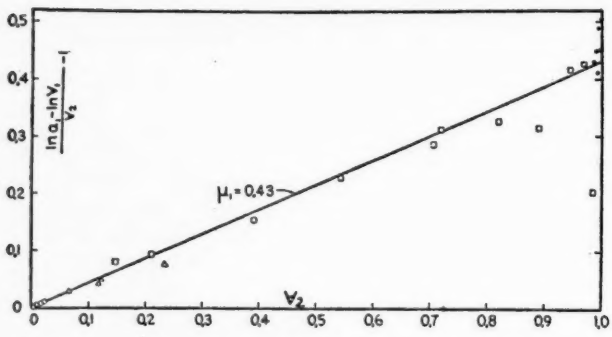

FIG. 9.—Rubber-benzene system (25° C), from data of Gee and Treloar[18].
○ Osmotic pressure.
△ Equilibrium against triolein.
□ Direct manometric method.
● McLeod gage method.

As Figure 9 shows, a constant value of μ_1, represented by the straight line, agrees with the experimental observations on the rubber-benzene system over the whole range of composition, within or nearly within the probable experimental error. (The scattering of the experimental points at high values of V_2 is due partly to the impossibility of reading the coördinates of the points on the published graphs accurately; the numerical data were not published. One might expect slightly low values at high rubber concentrations, however, as a result of failure to obtain equilibrium.)

TABLE I

VALUES OF μ_1 FOR VARIOUS SYSTEMS

System	μ_1	Temperature (° C)	Reference citation
Rubber			
Benzene + 10% C_2H_5OH	0.26	25	19
Carbon tetrachloride	0.28	15–20	10
Camphor	0.29	180	17
Cymene	0.33	15–20	10
Cyclohexane	0.33	6.5	8
Tetrachloroethane	0.36	15–20	10
Chloroform	0.37	15–20	10
Cumene	0.38	15–20	10
Light petroleum	0.43	25	9
Acetylene dichloride	0.43	15–20	10
Toluene	0.43–0.44	27	7
Benzene	0.43–0.44	7–40	20
Chlorobenzene	0.44	7	21
Thiophene	0.45	15–20	10
Carbon disulfide	0.49	25	12
Amyl acetate	0.49	25	19
Benzene + 15% CH_3OH	0.50	25	19
Ether	0.55	15–20	10
Ethylene chloride	0.62?	15–20	10
Gutta-percha			
Carbon tetrachloride	0.28	27	7
Toluene	0.36	27	7
Benzene	0.52	25	9
Balata-toluene	0.36	27	7
Hydrorubber-toluene	0.45	27	7

The value of μ_1 would be expected to vary somewhat with the temperature. In the case of the rubber-benzene system, this variation is very slight, as indicated by the fact that experimental results obtained at three different temperatures agree reasonably well with the same straight line (Figure 8). From Gee and Treloar's measurements of osmotic pressure at 30.6° and at 8.8–9.95° C, one can compute an average value of $d\mu_1/dT$ of about -0.0002. The higher the temperature, the smaller the value of μ_1. Considerably larger values of the temperature coefficient would be expected for many other systems.

The swelling pressure data on rubber gels containing ethylene chloride indicate an increasing value of μ_1 with increasing concentration (Figure 5). This may perhaps be real; it seems more likely, however, that the experimental data are in error. The swelling pressure is over 5 atmospheres at the highest concentration.

ACTIVITY CURVES FOR RUBBER-BENZENE SYSTEM

Figure 10 shows, for the rubber-benzene system, the enormous departure of the activity-mole fraction curve from Raoult's law. In addition to the

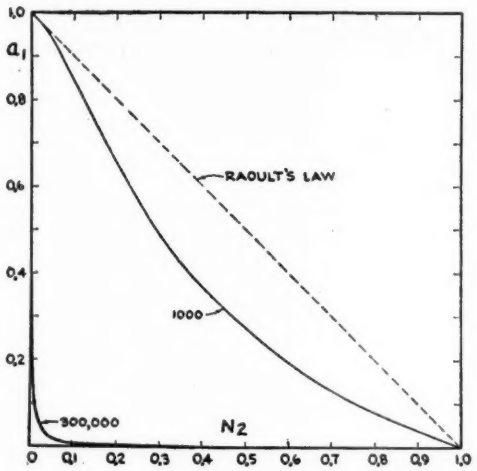

FIG. 10.—Activity as a function of mole fraction for rubber-benzene system ($\mu_1 = 0.43$).
Heavy curve: molecular weight = 300,000.
Light curve: molecular weight = 1,000.

heavy curve, drawn for a (number-average) molecular weight of 300,000, corresponding approximately to ordinary unfractionated rubber solutions, a curve is shown for a fraction of very low molecular weight (1000). Figure 11 gives the corresponding curves for the activity as a function of volume fraction. Similar curves can be readily drawn for other molecular weights and for other systems, once μ_1 has been determined.

Figure 12 shows the activity *vs.* volume fraction curves for certain arbitrary values of μ_1, with the size of the "solute" molecules (component 2) assumed to be infinitely large relative to the size of the solvent molecules. (This state of affairs may be assumed to exist in any gel.) As previously pointed out[22] the curves corresponding to values of μ_1 greater than 0.5 have a double inflection,

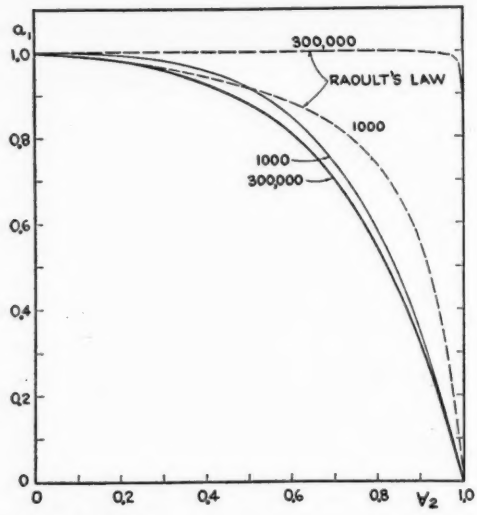

FIG. 11.—Activity as a function of volume fraction for rubber-benzene system ($\mu_1 = 0.43$).
Heavy curve: molecular weight = 300,000.
Light curve: molecular weight = 1,000.

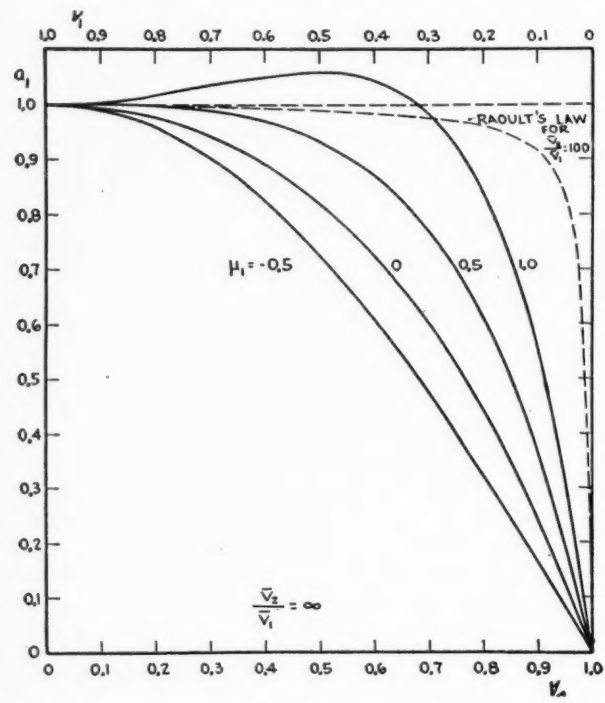

FIG. 12.—Activity as a function of volume fraction for a "solute" (*e.g.*, rubber) of infinite molecular weight (a gel), for different values of μ_1.

indicating a separation of phases. Except when μ_1 is very close to the limiting value, one phase is practically pure solvent; the other consists of the high-molecular-weight component (rubber) containing an amount of the low-molecular component determined by the concentration at which its activity equals unity.

CONCLUSION

Although the data presented suffice to show the general applicability of our theoretical equations to rubber systems, large gaps in our knowledge obviously remain. In particular, it would be desirable to have more data on systems having large μ_1 values.

ACKNOWLEDGMENT

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USF, A NEW CRUDE RUBBER *

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In preparing USF rubber by the preferred method, a field latex is preserved with formaldehyde as soon as possible after tapping. This chemical is effective in quickly and thoroughly stopping bacterial and enzymatic changes in the latex (Table I). Thus one of the most important sources of variability is

TABLE I

DEATH RATE OF BACTERIA IN LATEX CONTAINING FORMALDEHYDE

	Bacteria (cc.)
Fresh latex	21,000,000
Latex 1 hour after formaldehyde addition	<1,000
3 hours after formaldehyde addition	0
10 days after formaldehyde addition	0

eliminated at the start. The preserved latex is transported to the USF rubber plant and emptied into a tall settling tank; there it is allowed to stand for 48 hours for sand, dirt, and natural sludge components to separate. At the end of this time the supernatant liquid is withdrawn into a blending tank, and another charge is introduced into the settling tank. This process is repeated until the blending tank is filled. Then a fraction of the well-mixed latex from this tank, equal to a charge added from the settling tank, is removed for processing. The latex to be processed is highly diluted, acid is added, and the whole mass is stirred. Fine flocs form on standing and rise to the surface, leaving a clear yellow serum. This is withdrawn, and the flocculates are washed by the further addition of water. The washed flocs are transferred through a pipe to the coagulating tanks normally used for preparing sheet rubber. The flocs have now become sufficiently destabilized, so coalescence to a slab of coagulum may occur by simple standing at air temperature. However, faster coalescence is obtained by brief mild treatment with steam. The coalesced slab is removed and passed through mills for the production of crepe or sheet. The wet rubber is hung up to dry in a conventional dryhouse. Finally the dried rubber is heavily compressed and shipped in rubber-wrapped bales. This process is described in the flow sheet of Figure 1.

PRINCIPLES OF THE PROCESS

Preservation.—The first principle is adequate preservation as soon as the latex is tapped; this is accomplished at present by means of formaldehyde. The exact concentration is not critical. However, the facts indicate that the greater the amount of formaldehyde used, the better the product. By means of this preservative, a number of results are attained:

1. Bacterial and enzymatic actions and the biochemical changes produced by them are rapidly stopped and cannot recur during conversion of the latex to solid rubber.

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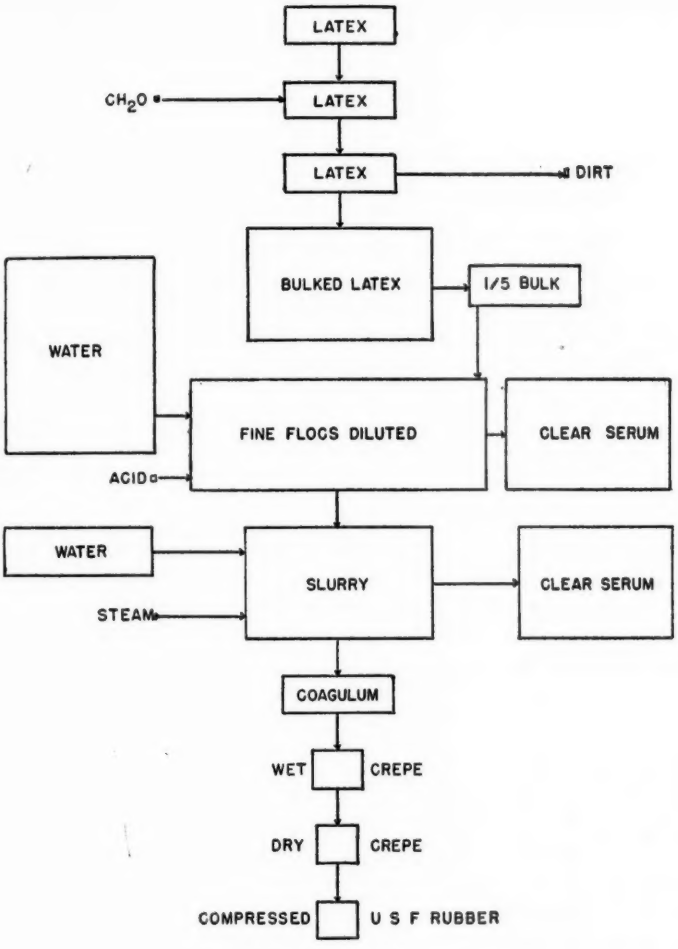

FIG. 1.—Flow sheet of USF rubber process.

2. The preserved latex thereby made is sufficiently stable to keep and handle throughout the entire process.

3. Latex containing formaldehyde is almost completely resistant to oxidation.

4. Formaldehyde reacts with the latex components, on standing in the latex, in such a way as to produce stable flocs after addition of acid.

5. Combined formaldehyde has been shown to be present in definite amounts in USF rubber received in the United States[1].

6. A rubber of easy breakdown and improved flex-cracking characteristics is obtained.

7. The cost of this method of preservation is low.

Bulking.—The preserved latices from which foreign materials have been removed by settling are combined in such a way as to produce a bulk held in

a definite total solids range. This bulk is built up over a period of time, and is kept as such with additions and withdrawals for as much as two or three months. Under these conditions variability due to estate, clone, seedling, soil, time of tapping month, or total solids of starting latex is compensated for. The result is a rubber of improved uniformity.

Flocculation.—When formaldehyde latex is treated with acid, stable aggregates are formed. These aggregates make possible thorough washing and ready creaming of the flocculated material, followed by removal of clear serum. This results in production of rubber low in water-soluble constituents. Stability of the aggregates may be produced by formation of a protecting body by interaction of formaldehyde with some of the latex components.

It is important to mention another point—namely, control of pH in the preparation of USF rubber. Figure 2 shows the type of curve obtained when

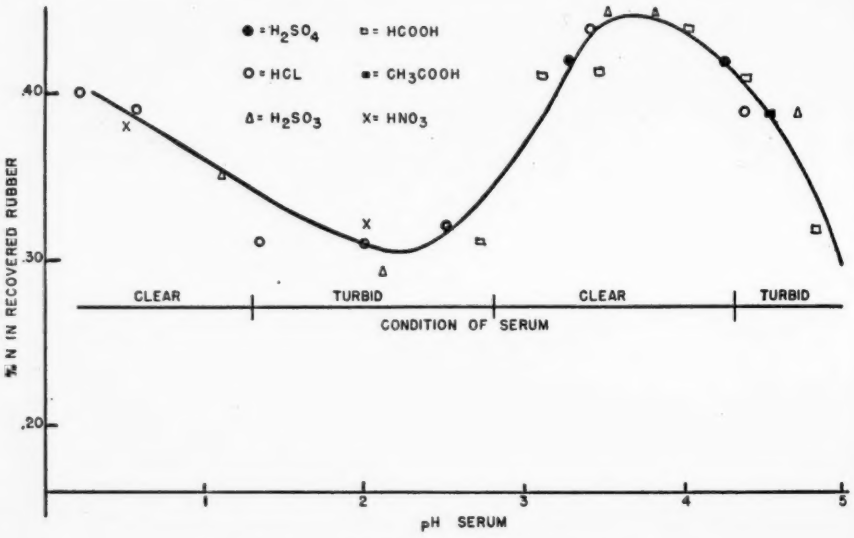

FIG. 2.—Nitrogen content of rubber *vs.* pH of serum.

the nitrogen content of rubber is plotted against the pH of serum recovered. There are definite maxima and minima, depending on the pH of the serum, which are substantially independent of the kind of acid used. For example, in the pH band 2.8 to 4.3, clear serum results (Figure 3), and rubber of maximum nitrogen is obtained. Above pH 4.3, turbid serum and rubber of lower nitrogen content are produced. Below pH 2.8 and down to pH 1.3, turbid serum and rubber of lesser nitrogen content are obtained once more. Further addition of acid (lowering the pH below 1.3) again produces clear serum and rubber of high nitrogen content. Six different acids were used in these tests, and the results fall substantially on the smooth curve of Figure 2. In accordance with this regularity of behavior, acid is added to produce a correct serum pH. This fact, coupled with the establishment of preserved latex bulk in a given total-solids range, fixes the amount of protein precipitated on the aggregates in a very narrow range. This control of nitrogen content contributes to the uniformity in the chemical and physical characteristics of this new crude.

Coalescence.—The thoroughly washed flocs are transferred through a pipe to coagulating tanks ordinarily used in the preparation of sheet rubber. Sufficient stability remains in the flocs to permit this transfer. On standing for some time at room temperature, these aggregates are able to coalesce to a compact coagulum. To expedite the process, however, steam is introduced

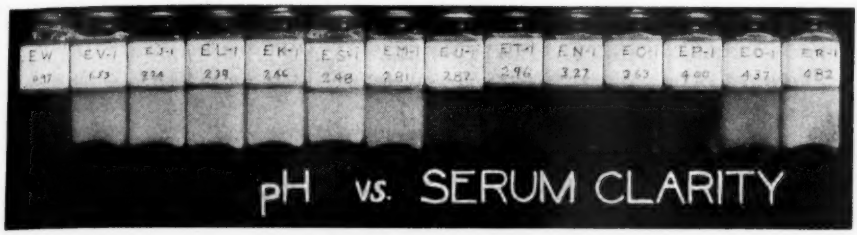

FIG. 3.—Effect of pH on serum clarity.

directly into the tanks, and the temperature is mildly elevated. This steaming is so conducted as to allow time for insertion of the usual dividers before coalescence occurs. All during this period the system is thoroughly protected from spoilage by the continued presence of a sufficient concentration of formaldehyde as well as by the presence of acid. After cooling, the coagulum is removed to mills and is converted either to sheet or crepe, as desired. As practically all water-soluble material has been removed, only a minimum of manipulation on the mills is necessary. This contributes both to a low processing cost and to quality advantages in the rubber.

Drying.—The milled coagulum is now dried by conventional methods—that is, by hanging in the crepe dryhouse. If sheet is desired, the rubber is

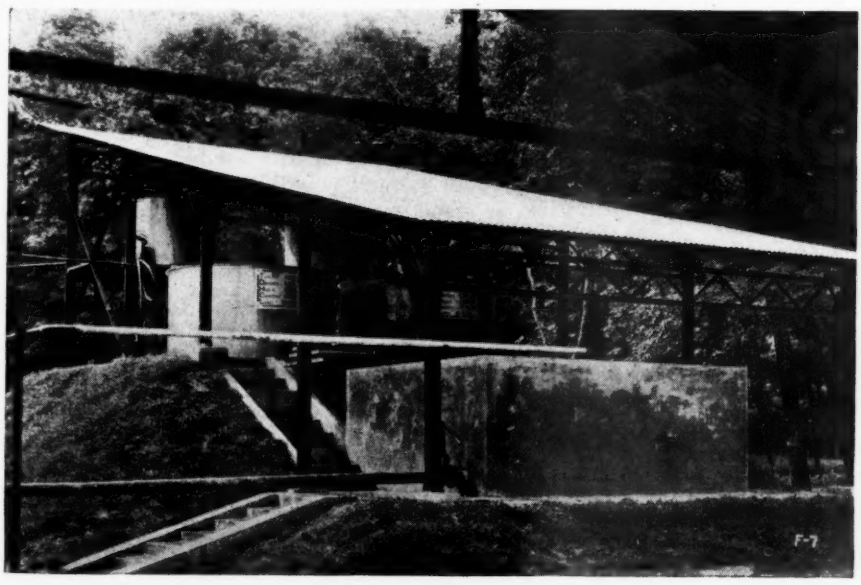

FIG. 4.—Settling, bulking, and flocculating tanks at a USF rubber plant.

dried in a current of warm air (120° F), without smoke. No smoke is used in the preparation of USF rubber sheet, and another source of variability is thus excluded[2]. Under the conditions of drying practiced, mould is not encountered.

Plant.—Figure 4 shows the settling, bulking, and flocculating tanks of a USF rubber plant at successively lower levels. After the flocculated rubber particles are washed, they are transferred, through the pipe leading to the left, to ordinary sheet coagulating tanks for coalescence.

CONTRAST WITH PRESENT METHODS

In present methods for the preparation of sheet or crepe, preservatives are used only as anticoagulants when necessary, and not for the constructive purposes employed in the preparation of USF rubber. The latex may stand for varying lengths of time before the coagulating acid is introduced. During this interval, all sorts of microörganism and chemical changes, including oxidation, can occur; it is quite possible that such changes are not completely arrested even by the addition of the acid. Because of rapid spoilage of the latex, it is almost impossible to build up a bulk sufficient for either adequate settling out of foreign material or proper blending of latices from different sources.

The addition of acid to latex which has not been preserved with formaldehyde results in the formation of unstable aggregates. These cohere to form a mass of coagulum within a relatively short time. Therefore the effectiveness of washing rubber produced by the usual processes depends, first, on the original dilution of the unpreserved latex and, secondly, on the washing given the mass of coagulum.

In the case of sheet, practically all washing is done in the dilution step; the amount in the sheeting operation is small. In the case of crepe, washing is by dilution, and is continued as the coagulum is passed repeatedly through the mill rolls. Thus crepe rubber is somewhat more thoroughly washed than sheet, but at the expense of the severe kneading effect of the heavy crepe mills. This manipulation is costly. Furthermore, it introduces two hazards: (1) contamination from the metal rolls, and (2) alteration of the rubber hydrocarbon if exposed to heavy pressure, strain, and oxidation by the air while being worked.

In contrast to the foregoing, the USF process is conducted under such conditions as to confine the sources of variability within much narrower limits than in the conventional sheet or crepe process.

GENERAL PROPERTIES

The basic difference between USF rubber and market grade crudes lies probably in the effective preservation by formaldehyde of the rubber hydrocarbon in its original unspoiled condition throughout the entire period of preparation. This method of preservation prevents changes in the latex and in the coagulum due to microörganism or oxidative actions. USF rubber may be dried in crepe form. It may be dried equally well in sheet form at a slightly elevated temperature without smoking. Mould is not encountered in properly prepared USF rubber crepe or sheet. The formaldehyde treatment probably retards the rapid changes in various properties observed in ordinary sheet or crepe during and after shipment.

USF rubber is soft and shows good flex-cracking characteristics. These properties are obtained probably by the use of formaldehyde, by reduction in

manipulation on the heavy creping mills, and by elimination of smoking. All of these factors contribute to the prevention of damage to the rubber. USF rubber is clean because the latex is not only strained as usual but is further purified by a sedimentation step. This crude rubber is uniform and light in color because of the preservation treatment, blending, in a specified total solids band, thorough washing of the flocs, and elimination of smoking.

The washing step removes the major part of the water-soluble, nonrubber components present in formaldehyde-preserved latex. This results in a rubber low in ash and acetone extract. For every pound of USF rubber purchased, then, as much as one per cent more of rubber hydrocarbon is available than in the average market grade sheet.

The fact that USF rubber is less altered during its preparation than sheet or crepe is indicated by certain other properties. For example, it is more soluble in Skellysolve (a naphtha solvent) at 70° C than is No. 1 smoked sheet. It has a lower Mooney plasticity immediately after preparation than comparable smoked sheet. The spread between the plasticities becomes even greater when USF rubbers and smoked sheets are examined in this country. Even when, after long storage, USF rubber has attained a Mooney value comparable to that of the softer smoked sheet, it still breaks down with a far lower power consumption. Furthermore, USF rubber is softer by the Mooney plastometer than smoked sheet after equivalent breakdown treatment on the mill. USF rubber shows slightly faster rates of vulcanization with sulfur chloride than does pale crepe. It also vulcanizes slightly faster in certain commercial compounds than smoked sheet. (Minor compounding adjustments are adequate in most cases to take care of these small differences in rate of cure.) The point made here, however, is that USF rubber contains a hydrocarbon of different and valuable chemical and physical properties compared with those found in the usual grades of crude rubber.

SOFTNESS

One of the outstanding merits of USF rubber is its lower viscosity and greater ease of breakdown than other crudes. The average Mooney plasticity

TABLE II

MEAN VALUES IN TWO EXPERIMENTS COMPARING USF RUBBER AND SMOKED SHEET

Rubber	Where tested	No. of samples	Ash (percentage)	Nitrogen (percentage)	Acetone extract (percentage)	Mooney plasticity	Green tensile strength[a] (lbs. per sq. in.)
USF	Sumatra	15	0.12	0.37	2.82	66.2	2998
S. S.	Sumatra	15	0.30	0.42	3.45	70.8	3120
USF	America	19	0.11	0.40	2.84	70.4	2695[b]
S. S.	America	15	0.20	...	3.16	90.0	2268
			Mean deviation from mean per individual sample				
USF	Sumatra	15	0.017	0.009	0.16	0.9	141
S. S.	Sumatra	15	0.039	0.027	0.19	1.5	358
USF	America	19	0.012	0.013	0.25	3.4	174
S. S.	America	15	0.049	...	0.20	12.3	303

[a] A.C.S. formula, vulcanized 40 minutes at 21 pounds.
[b] 1.5 parts stearic acid.

(Table II) of fifteen samples of USF rubber compared with fifteen samples of smoked sheet, all prepared and tested at the same time at our plantations, shows that USF is definitely softer than smoked sheet. The contrast is still

more striking (Table II) between data on nineteen USF and fifteen smoked sheet shipments tested in the United States. In this case the USF rubbers had a mean plasticity value of 70.4, and the smoked sheet, a mean of 90.0. Not only is there a wide spread between the two rubbers but also a far sharper rise in plasticity in the smoked sheet than in the USF rubber.

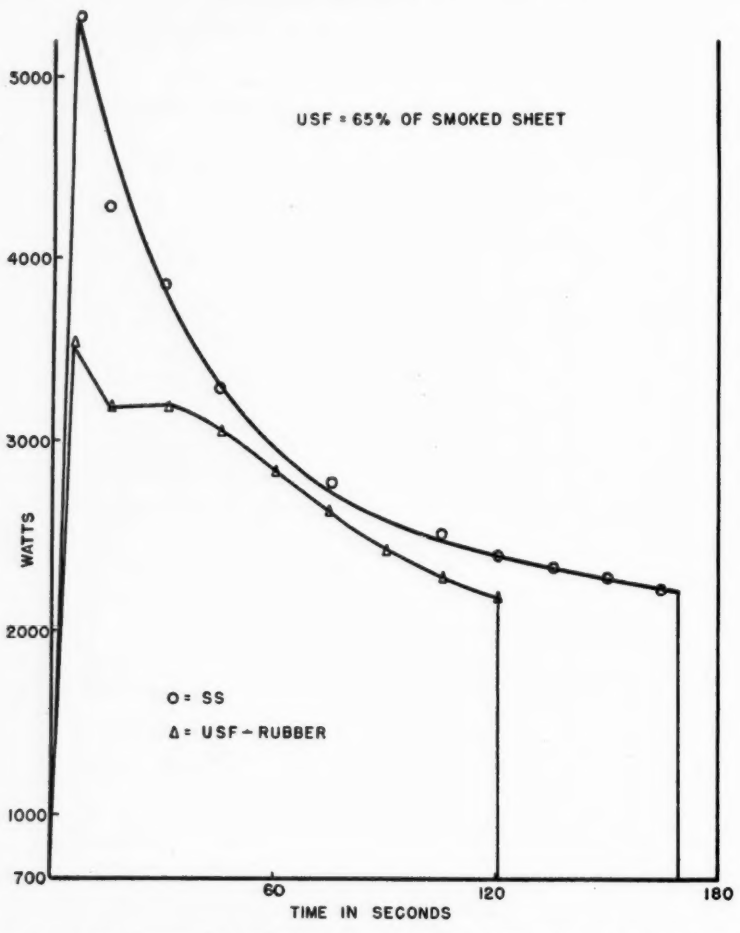

FIG. 5.—Power consumption for mill breakdown at 200° F of USF rubber and smoked sheet.

Softness is shown in Figure 5, where the power consumed in the breakdown of USF and of smoked sheet is compared. The tests were carried out with a 600-gram batch on a 6-inch laboratory mill operated at 200° F, on a 220-volt circuit. Readings were taken in amperes and plotted as watts *vs.* time in seconds. The end-point of the test was the time the rubber became smooth on the mill. The data presented are the mean values of eight shipments of USF rubber and nine lots of smoked sheet of average hardness. The area under the curves, a measure of power consumption, has been found to be for USF rubber only 67 per cent of that for smoked sheet. If the area corre-

sponding to the power consumed by the idling mill is eliminated, the power consumption of USF rubber is 65 per cent that of smoked sheet. Thus, USF rubber as received in this country is substantially softer than the average smoked sheet, not only in terms of plasticity, but also of actual power consumption. This is an important point to those concerned with the plasticization of crude rubber.

The greater softness of USF not only exists in the crude material, but also carries over into the compounded unvulcanized rubber. Table III indicates

TABLE III

COMPARISON OF USF RUBBER AND SMOKED SHEET IN A STANDARD TREAD FORMULA

		Unvulcanized					Vulcanized 35 min. at 48 lb.			
		Min. on mill		Mooney plasticity				Lb. per sq. in.		
Rubber	Code No.	Breakdown	Total	Crude	Compounded	Milled 5 min. at 160° F	T-50 test	Modulus at 500%	Original tensile	Aged tensile[a]
Smoked sheet	SB	3.2	8.7	102	113	92	− 9.3	3400	4300	2500
	RP	3.4	8.6	97	116	91	−11.7	3200	4000	2500
	RM	3.0	7.8	98	107	94.5	− 8.9	3100	3900	2400
	TC	2.8	7.6	97	...	...	−11.4	...	...	...
Mean	...	3.1	8.2	99	112	93	−10.3	3233	4067	2467
USF rubber	TA	1.7	6.9	71	...	...	−13.2	...	...	...
	RN	2.1	6.8	69	100	82	−13.6	3200	3800	2500
	RQ	2.3	7.9	73	102.5	83	−13.7	3100	3800	2500
	SF	2.0	7.5	68	96.5	86	−13.0	3300	4200	2500
Mean	...	2.0	7.3	70	100	84	−13.4	3200	3933	2500

[a] After 96 hours in oxygen bomb.

the shorter time required to breakdown and to mix a standard tread formula from USF rubber compared with smoked sheet. Likewise, the Mooney values for the crude as well as those for the compounded stock and for the stock after 5-minute milling are definitely lower where USF rubber is used.

CLEANNESS AND COLOR

The cause for the cleanness of USF rubber is evident from the description of the process. Dirt figures shown in Table IV are further confirmation of this

TABLE IV

ADVANTAGES OF USF RUBBER OVER SMOKED SHEET

	USF Rubber	Smoked Sheet
Power consumption (watts)	67	100
Mooney plasticity	65–75	66–112
Ash (percentage)	0.09–0.12	0.12–0.33
Nitrogen (percentage)	0.37–0.42	0.35–0.56
Acetone extract (percentage)	2.60–3.20	2.70–3.68
Dirt (percentage)	0.005 (av. of 19 samples)	0.059 (av. of 4 samples)
Color	Light (resembles pale crepe)	Dark
Uniformity	Obtained by formaldehyde preservation, bulking of latex, new method of coagulation, washing	Lacking because of rapid spoiling of unpreserved latex, cannot be bulked, is smoked

quality compared with several random tests on smoked sheet. According to certain factories using USF rubber, substantial savings have been realized because of the comparative freedom of this material from sand, wood, bark, fibers, and like components frequently present in market grades of crude.

The reason for the light color is also readily evident. No smoking is used and spoilage of the latex is avoided, as a result of early and effective preservation. Less darkening was observed in USF rubber in a 30-minute factory milling test than in a parallel test on pale crepe. Furthermore, USF has been shown to be satisfactory when introduced into light-colored goods or transparent stocks.

VULCANIZATION

Stress-strain and T-50 tests.—Both in a standard tread formula (Table III) and in the A. C. S. formula (Table II), USF rubber has cured so that modulus and tensile strength are but little different from smoked sheet. The T-50 data (Table III) indicate that USF rubber is slightly faster vulcanizing than smoked sheet. In other compounds, also, USF rubber has been found to vulcanize somewhat faster; however, it shows a marked advantage in uniformity of the vulcanizate over smoked sheet.

Aging.—USF is a good-aging rubber, as shown by tensile strength values on several accelerated tests on different stocks (Table V).

TABLE V

AGING OF USF RUBBER

Aging treatment	Type stock	Cure		No. samples	Tensile (lbs. per sq. in.)	
		Min.	Lbs.		Aged	Green
Geer oven (12 days, 70° C)	A. C. S.	40	21	15	3136	2998
O_2 bomb (48 hrs., 300 lbs., 70° C)	A. C. S.	40	21	19	3000	2695
O_2 bomb (96 hrs., 300 lbs., 70° C)	Tread	35	48	3	2500	2933
Autoclave (6 hrs., 70 lbs. air, 275° F., 50% stretch)	Inner tube	10	53	3	2000	3567

Flex cracking.—DeMattia flex-cracking resistance is 34 per cent better in the USF rubber now being produced commercially than in smoked sheet (Table VI). In experimental USF rubbers, prepared from latex of increased formaldehyde content, the advantage in flex-cracking resistance has been raised to 62 per cent over that of smoked sheet (Table VI).

TABLE VI

FLEX-CRACKING RESISTANCE

No. of shipment	DeMattia flex-cracking (kilocycles)		Improvement (percentage)	Sample No.	DeMattia flex-cracking (kilocycles)		Improvement (percentage)
	Smoked sheet	Commercial USF			Smoked sheet	Exptl. USF	
1	196	225	15	1	248	432	74
2	230	353	53	2	253	409	62
3	202	288	43	3	226	405	79
4	185	205	11	4	330	471	43
5	233	332	42	5	256	390	52
6	228	319	40				Mean 62
			Mean 34				

UNIFORMITY

Uniformity in crude rubber has been a problem ever since plantation rubber became our major source of crude rubber. Hastings and Rhodes[3] stated that fine Para was considered more uniform than plantation crude rubber in 1914. They quoted other workers to the effect that little improvement had been made in this matter of variability by 1938. They also stated that the uniformity of fine Para was due to the relatively uniform removal of nonrubber components by washing. Some rubber men believe that crepe rubber is more uniform than sheet; crepe also has had more washing during the course of its preparation.

The fact that USF is thoroughly and uniformly washed under favorable conditions (namely, in the finely flocculated state), together with the method of preservation, the blending procedure, and the elimination of smoking, gives fourfold assurance of uniformity. These conditions should be effective in eliminating criticism such as that quoted by Hastings and Rhodes[3]: "It seems clear that this series of experiments has proved that the variation which is apparent in raw rubber is still apparent in the finished tyre".

Van Dalfsen[4] reviewed the subject of variability of rubber in detail, including a complete bibliography. His recommendation for the preparation of special rubbers for special purposes is a means of making progress from one direction. But the USF process offers a method of obtaining greater uniformity and quality in the general supply of crude rubber, the "mass product" in contradistinction to special rubbers of smaller consumption for particular purposes.

The uniformity of USF rubber is shown in Table II. The ash, nitrogen, and acetone extract values are lower than those in smoked sheet. Furthermore, the deviations of the individual values from the mean are decidedly less for ash and nitrogen than in smoked sheet. The plasticity data in Table II not only show smoked sheet to be harder than USF in the East and still more so in this country, but also indicate that the deviation in the plasticity of smoked sheet is greater at the plantations than that of USF rubber. When examined in the United States, USF showed somewhat greater variability than it did when freshly made; in contrast, when smoked sheet was examined in this country, it revealed an eightfold increase in plasticity variability.

The vulcanization data obtained on USF rubber and smoked sheet in the East show but little difference in mean tensile properties in the 40-minute time of vulcanization of the A. C. S. formula. Smoked sheet tested in the United States had a decidedly lower mean tensile than either of the above. The USF rubber tested in this country was not directly comparable to the smoked sheet, inasmuch as the stearic acid content of the A. C. S. formula had been increased.

The T-50 values of the four USF rubbers in the tread formula (Table III) are almost identical. Three series of fifteen, nineteen, and twenty-four USF rubbers gave mean 700 per cent modulus figures in the A. C. S. cure of 1380, 1440, and 1404 pounds per square inch, respectively. These data indicate strikingly the uniformity in the cure of USF rubber.

A. C. S. tensiles of USF fall in a narrower range than those of smoked sheet because of the greater uniformity of the new rubber. The deviation values in the USF and smoked sheet series (Table II) average 331 for smoked sheet but only 159 for USF rubber.

THEORY

Throughout the discussion, it has been stressed that the superior properties of USF rubber may be correlated with the production of an unspoiled and unpolymerized hydrocarbon different from that found in ordinary market grades. Greater softness, greater solubility, improved flex-cracking, faster rate of vulcanization, elimination of smoking, reduction of creping, heavy compression for shipment, the presence of formaldehyde as enzyme poison, antioxidant, and possible polymerization retarder—all these factors support the suggestion that USF may contain a more unsaturated rubber molecule than is present in usual market grades.

ACKNOWLEDGMENT

The writers wish to express their appreciation of the cooperation and help of W. E. Cake, director of the Research Department of the United States Rubber Plantations, and of his efficient staff.

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OXIDATION OF RUBBER AND ITS COLLOID-CHEMICAL RESULTS *

R. HOUWINK

There is a very comprehensive literature on the oxidation of rubber, but in it many contradictory observations by various authors are found. Formerly, when technologists had only a summary view of the colloid chemistry of rubber, few critical interpretations were based on it, and it is therefore not surprising that there are now so many conflicting opinions in this field.

A cardinal error frequently made in this connection is that in the experiments described it was stated that oxygen was absent. But it has proved extremely difficult to render rubber absolutely free of oxygen, and it must therefore be assumed that in most of these earlier experiments traces of oxygen, although sometimes very slight, actually were present[1]. It is now known that, in degradation and polymerization processes of high molecular substances, very slight traces of an impurity may have considerable influence on physical properties. Thus if 0.003 per cent of *p*-divinylbenzene is added to soluble polystyrene, the latter may become insoluble as a result of bridging between the long-chain molecules in a few places[2]. On the other hand, the viscosity of rubber can be considerably reduced by traces of oxygen if the O atoms sever the long rubber chains in the middle. In Staudinger's viscosity rule[3]:

$$\eta_{sp} = KMc \qquad (1)$$

η_{sp} = specific viscosity = $\dfrac{\eta - \eta_0}{\eta_0}$

η = viscosity of solution

η_0 = viscosity of solvent

K = constant

M = molecular weight

c = concentration of basic molecules (structural units)

The viscosity is proportional to the average chain length (expressed by M). If a substance consists of a few long chains, less oxygen is needed to break each of these in half than if it consisted of many small chains. In the first case, therefore, the effect per gram of oxygen is much greater. Thus with a molecular weight of 150,000 for rubber, 0.002 per cent oxygen would, according to Scheme 1b, Table 1, be sufficient for severance[4]; whereas a molecular weight of 150 would require 2 per cent of oxygen. Accordingly, Asano's experiments[5] in which rubber "was treated in an oxygen-free atmosphere" but nevertheless was found to contain 3.35 per cent of oxygen, must be regarded as questionable. It is likely that in this percentage there was enough free oxygen present to have had a powerful degradation action.

Because of the marked effect of mere traces of oxygen, it is easily understood why van Rossem[6] at first concluded that oxidation was a secondary process preceded by depolymerization. The limited exactitude of investigation methods at that time did not permit the detection of the tiny traces of oxygen which initially cause a considerable reduction of η (depolymerization),

* Reprinted from the *India Rubber World*, Vol. 107, No. 4, pages 369–377, January 1943. This paper represents Communication No. 22 of the Rubber Stichting, Delft, Holland.

TABLE 1

SOME POSSIBILITIES FOR POLYMERIZATION AND DEPOLYMERIZATION OF RUBBER MOLECULES; EXPECTATIONS REGARDING PHYSICAL RESULTS

Scheme	Order of probability	Supposed reaction	Mechanism	Physical results: On solid rubber	Physical results: On rubber in solution ($\eta sp = KMc$)
1a	1	$\underbrace{-CH_2-CH=CMe}_{R_1}-CH_2-\underbrace{CH_2-CH=CMe-CH_2-}_{R_2} + 3\,O \rightarrow R_1-CHO + R_2-CHO + H_2O$ oxygen depolymerization	Molecule severed by O_2	Becomes softer	Decreases viscosity
1b	1	$-CH_2-CH=CMe-CH_2- + 2\,O \rightarrow -CH_2-CHO + O=CMe-CH_2-$ oxygen depolymerization	Molecule severed by O_2	Becomes softer	Decreases viscosity
2	3	$\underbrace{-CH_2-CH=CMe}_{R_1}-CH_2-CH_2-CH=\underbrace{CMe-CH_2-}_{R_2} \rightarrow R_1-CH=CH_2 + H_2C=R_2$ true depolymerization	Molecule severed without O_2	Becomes softer	Decreases viscosity
3a	3	$\begin{matrix}-CH_2-CH=CMe-CH_2- \\ -CH_2-CH=CMe-CH_2-\end{matrix} + O \rightarrow \begin{matrix}-CH-CH=CMe-CH_2- \\ \vert \\ -CH-CH=CMe-CH_2-\end{matrix} + H_2O$ dehydrogenation	Bridging between two molecules under influence of O_2	Becomes harder	First decreases* viscosity; then increases it
3b	3	$\begin{matrix}-CH_2-CH=CMe-CH_2- \\ -CH_2-CH=CMe-CH_2-\end{matrix} + O \rightarrow H_2O + -CH_2-CH=CMe-\underset{\vert}{CH}-CH-CH=CMe-CH_2-$ dehydrogenation	Bridging between two molecules under influence of O_2	Becomes harder	Increases viscosity
4	2	$\begin{matrix}-CH_2-CH=CMe-CH_2- \\ -CH_2-CH=CMe-CH_2-\end{matrix} + 2\,O \rightarrow \begin{matrix}-CH_2-CH-CMe-CH_2- \\ \vert \quad \vert \\ O \quad O \\ \vert \quad \vert \\ -CH_2-CH-CMe-CH_2-\end{matrix}$ bridging by oxygen	Bridging between two molecules by O_2	Becomes much harder	Decreases* viscosity at first; then increases it
5	1	$\begin{matrix}-CH_2-CH=CMe-CH_2- \\ -CH_2-CH=CMe-CH_2-\end{matrix} \rightarrow \begin{matrix}CH_2-CH-CMe-CH_2 \\ \vert \quad \vert \quad \vert \\ CH_2-CH-CMe-CH_2\end{matrix}$ cyclization (polymerization)	Bridging between two molecules without O_2	Becomes much harder	Decreases* viscosity at first; then increases it

* If the molecules were coupled as in Scheme 3b, the viscosity would increase constantly.

though at a later stage—when larger, analytically observable amounts of oxygen come into play—the change was relatively much smaller.

It is the author's opinion that well-grounded efforts to view the results of the oxidation of rubber in the light of modern colloid chemistry are lacking in the comprehensive literature referred to. Recent, detailed summaries on the oxidation problem[7] do exist, but the writer doubts whether these authors have realized with sufficient clarity to what colloid-chemical results polymerization and degradation processes in high polymer substances may lead.

It will be attempted to present such a consideration below. The influence of ozone will, however, be omitted, since its inclusion would lead to various complications[8]. It is not intended to give a complete review of the existing literature; for that the reader is referred to the sources[7].

STRUCTURE OF RAW AND VULCANIZED RUBBER

Before the influence of oxidation is discussed, it is desirable briefly to restate our present views on the structure of rubber. The well-known general assumption is that chain molecules built up of isoprene groups, as in Figure 1, are present in raw rubber.

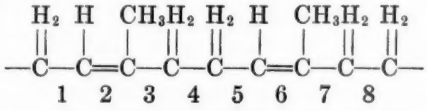


FIG. 1.—Polymerized isoprene (natural rubber).

Staudinger assumes that such chains have a degree of polymerization of 2,000 and, hence, have a molecular weight of 136,000; sometimes mention is found of still higher values[9], as, for instance, a molecular weight of 400,000.

A point for our consideration is that there is one double bond per isoprene group; it is also very important that the —C—C— bond indicated by no. 4, is assumed to be the weakest in the molecule. A prediction can be made, based on Schmidt's so-called *Doppelbindungsregel* (double-bond rule)[10], in which it is stated that in an olefin the first single bond following a double bond is strengthened, and the succeeding one weakened. If this rule is applied to the isoprene chain in Figure 1, it will be seen that the —C—C— bond no. 4, is weakened as a result of double bonds nos. 2 and 6. Thus there is a superposition of two weakening effects, and there is no doubt that bond no. 4 forms the weakest link in the chain. This is clearly seen in the dry distillation of rubber, where Midgley and Henne[11] conclude that the following ratio values for rupture are obtained for the various bonds:

	Bond			
	1	2	3	4
Distillation without addition of Mg, MgO, or ZnO	0.7	0	0.6	100
Distillation with addition of Mg, MgO, or ZnO	12.1	0	12.7	100

A very plausible representation[12] of how these chains together build up rubber is shown in Figure 2. The chains are irregularly intertwined, but in places they run more or less parallel, to form crystallites *K* locally. Coherence in these crystallites is obtained by feeble van der Waals bonds having an energy content estimated at a few kg. per cal. per mol., so that they easily melt when heated. Later the idea will be developed that in practice these structural forms presumably appear in only a very few instances, but that

complications due to net formations probably almost always take place (see Figure 3).

In vulcanized rubber it is at present generally assumed that the sulfur atoms are added to the double bonds, forming so-called bridging bonds between the rubber chains.

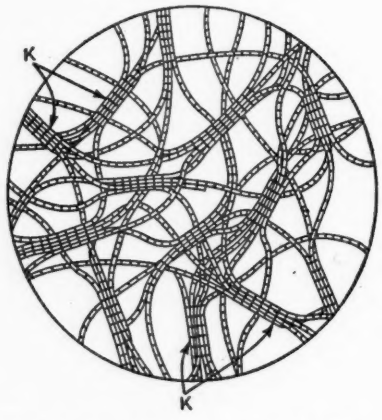


FIG. 2.—Chain molecular structure of rubber.
K = Crystallite.

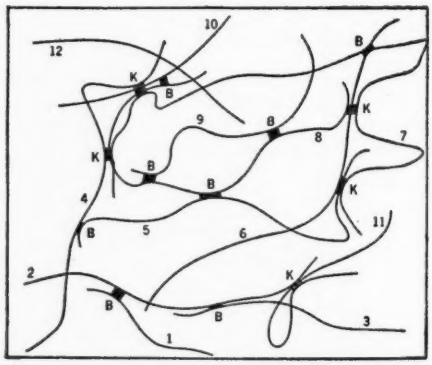


FIG. 3.—Assumed structure of vulcanized rubber.

The chain molecules are imagined to be coupled together at the places ■ B by a bridging bond. It is assumed that the chains 1, 2, and 3, for instance, are mutually connected, but are not attached to the network 4–10. In this way small aggregates (sol rubber) are obtained next to larger aggregates (gel rubber). It is possible that there are also loose chains (11 and 12) present. Besides the (chemical) bridge bonds, crystallite formation |||||| K, as in Figure 2, is also assumed. However, the combination K is weak (a few kcal. per mol) and is broken by gentle warming and by many solvents.

Figure 4 suggests various possibilities which may be divided into two groups: namely, intramolecular, *left*, and intermolecular bridging, *right* in the figure. It is perhaps possible that both types occur side by side, but that intermolecular bridging is always present. The latter hypothesis offers a satisfactory means of explaining such changes occurring during vulcanization as increase in tensile strength, hardness, temperature stability, and decrease

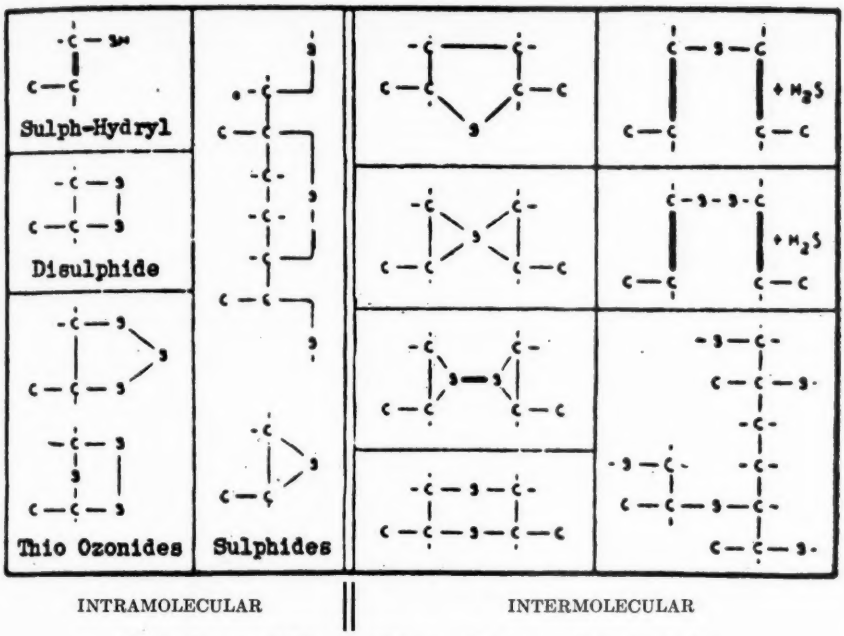


FIG. 4.—Some possibilities of bridging by sulfur as a result of vulcanization.

in plasticity. These changes become comprehensible if one considers that the highly energetic intermolecular bridges will oppose the sliding movement of the chains.

FACTORS WHICH PLAY A PART IN OXIDATION; STANDARDS OF JUDGMENT

If a complete study of the subject is to be made, unvulcanized as well as vulcanized rubber must be considered. Oxidation depends to a great extent not only on temperature, but also to an important degree on the effect of light.

In experiments where it has been attempted to investigate the effect of ultraviolet light alone, *i.e.*, when oxygen is excluded, a domain is entered where the uncertainty mentioned above concerning the reliability of the experiments, frequently exists.

The viscosity in solution, which according to (1) is very sensitive to molecule length, may be selected as the chief criterion for judging the changes which occur. It is important to ascertain to what extent rubber is or is not completely soluble, for insolubility may indicate bridging between chain molecules and consequent formation of aggregates of macroscopic dimensions. Thus raw rubber is rendered insoluble by vulcanization. On the other hand, it may also indicate the presence of very long chain molecules, as is deducible from Brönsted's law[13]. The ratio of the amounts of solvent distributable between two fractions whose degree of polymerization is P and p, respectively ($P > p$), is:

$$\frac{C_P}{C_p} = e^{(P-p)\epsilon/RT} \qquad (2)$$

C = concentration

ϵ = conversion energy per base molecule.

The specific role of the solvent is expressed by the factor ϵ. In the case of polybutene, only the low polymerized fractions dissolve[14] in dioxane; the medium fractions also dissolve in ethylene chloride, and all fractions, up to the very highest, in benzene.

In the solid state, the tensile strength σ_{max} is the criterion, since it can roughly be stated that the cohesion between two chain molecules increases in proportion to the length of the chain, l.

$$\sigma_{max} = Kl \qquad (3)$$
$$K = \text{constant.}$$

That a maximum is here reached (see Figure 5) may be due to the fact that, beyond a certain chain length, the molecules no longer slide past each other, but break into pieces themselves. Increasing net formation also increases tensile strength, since it reënforces the mutual cohesion of the chains.

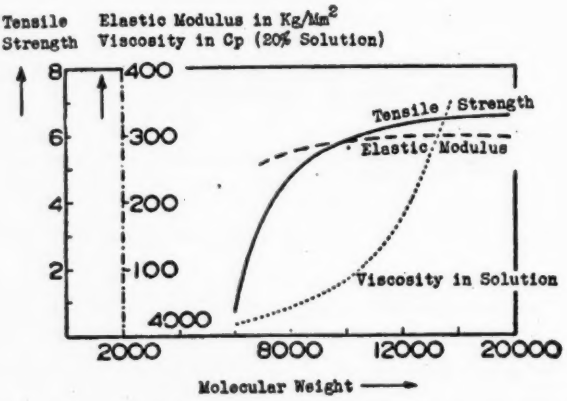


FIG. 5.—Changes in some physical properties of a vinyl polymerizate occurring with increasing chain length.

Other criteria in the solid state are elongation at break, which generally increases with greater chain length[15] and hardness which, on the basis of the observation made in connection with (3), is easily understood. However, hardness increases mainly in connection with net formation[16], because the latter, in particular, hampers the moving apart of the chains.

The tackiness of rubber in connection with oxidation is also an important criterion. Blake and Bruce[17] have shown that light and oxygen are necessary to produce tackiness, but that ultraviolet light or ozone is not.

An example[18] of the change which occurs in some of the properties, previously mentioned, when polymerization increases, is given in Figure 5 applied to a vinyl polymerizate. Conversely, it may be concluded from Figure 5 that severance of the chains is accompanied by deterioration in both tensile strength and viscosity. Supposing net fragments are present instead of chains, approximately the same picture is obtained as in Figure 5. For the viscosity, this follows from Equation (4), which will be discussed later; as to the tensile strength, an argument analogous to that used in discussing Equation (3) can be postulated for the decreasing cohesion. A difficulty in interpreting the observations on vulcanized rubber is the orientation required to appreciate the

connection between the amount of combined sulfur and the properties of the vulcanizate in such compounds where it is certain that no oxygen is present. Because of the great experimental difficulties, few measurements are available; therefore the starting point for the eventual explanation of the effect of oxygen on vulcanized rubber is not always unimpeachable. On the basis of analogies, it is, nevertheless, possible to develop various views with a reasonable measure of certainty.

Table 2 gives a rough picture of the results of oxidation. It shows in what general direction the properties of rubber change under the following conditions:

(*a*) If no oxygen or sulfur is present.

(*b*) Under the influence of oxygen alone.

(*c*) Under the influence of sulfur (vulcanization), and in the presence of some oxygen: namely, that which was dissolved in the rubber under the conditions of the experiment.

TABLE 2

ORIENTATION SURVEY OF THE CHANGES WHICH RUBBER UNDERGOES UNDER THE INFLUENCE OF FREE OXYGEN AND SULFUR

Property	Conditions	In the dark	In light
Viscosity in solution	Without O or S	Remains practically constant[19]	Increases; rubber becomes practically insoluble[20]
	With O	Decreases[21]	Decreases, but much more rapidly than in the dark. Remains soluble[22]
	With S	Rises during vulcanization; becomes insoluble	Rises, becomes insoluble[23]
Tensile strength in solid state	Without O or S	Remains constant	Rises
	With O	Declines; but under certain conditions may rise[24]	Same as in the dark
	With S	Rises; falls (effect O?); rises[25]	Same as in the dark
Hardness and tackiness	Without O or S	Remains practically constant[26]	Becomes hard and not tacky[5]
	With O	Becomes cheesy, then sometimes hard, sometimes tacky[27]	Becomes soft and tacky[28]
	With S	Becomes harder[26]	Becomes harder[26]

For the present the most important conclusion to be drawn from the table is that the solution viscosity always decreases as a result of the influence of free oxygen, and that tensile strength and hardness also usually decline. Under the influence of sulfur (vulcanization) the contrary is usually observed; hence it is permissible to say that the closely related elements, oxygen and sulfur, have opposite effects.

This question and Table 2 will be considered later.

POLYMERIZATION AND DEPOLYMERIZATION POSSIBILITIES OF RUBBER UNDER THE INFLUENCE OF OXYGEN

From Figure 1 it appears that sulfur in general effects such changes in rubber as may be compatable with the formation of intermolecular bridging. The increase in viscosity, which rapidly leads to insolubility, the mounting

tensile strength during vulcanization (see Figure 6), and the growing hardness, point in this direction. However, oxygen is strongly inclined to alter these properties in the opposite direction, and this point leads to the thought that oxygen has a greater tendency to depolymerization, *i.e.*, to a breaking down of the molecules, although the capacity for a polymerizing action is not to be excluded.

In Table 1 some schemes are given of reactions with oxygen which, on the strength of various experiences with highly polymerized substances, may be

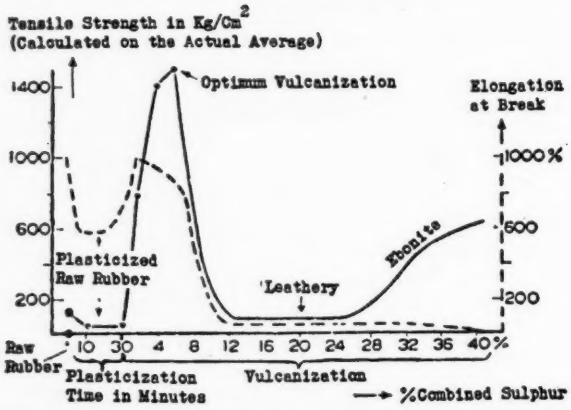


FIG. 6.—Change in tensile strength of vulcanized rubber during the manufacturing process. (The values are calculated on the actual surface during the tensile test[29].)

assumed to be admissible. Under 1a[30] and 1b are schemes of oxygen-depolymerization where the chain molecules are severed either in the weakest spot (4), as shown in Figure 1, or at the double bond. Both processes, if taking place in the middle of the molecule, would lead to a reduction by half of the viscosity and would render solid rubber more fluid. Both reactions possess a great measure of probability, as the second column indicates. Under 2 we find an example of true depolymerization, which therefore proceeds without oxygen, and which amounts to severance of the molecule in its weakest spot (4).

Schemes 3a and 3b represent dehydrogenation reactions attended by the coupling together of two molecules. It will depend entirely on the steric form which the final product assumes whether the viscosity decreases in the beginning (Scheme 3a; here two chains are practically united to one thicker one)[31] or increases (Scheme 3b). Ultimately η will increase in both cases, because increasing bridge-formation finally leads to insolubility. A minimum in the η-polymerization degree curve may, therefore, be expected here. Processes 3a and 3b both result in solid rubber becoming still firmer because the bridging that takes place between the chains hinders sliding of the molecules.

In Scheme 4 we see how a bridging action similar to that assumed for sulfur can also be attributed to oxygen. If this reaction runs its course, the final effect will be comparable with that in vulcanization. Here too, as in Scheme 3a, an initial decrease, followed by an increase in viscosity, may perhaps be expected.

Scheme 5 represents the cyclization reaction, which also leads to bridging between the chain molecules and which, therefore, is comparable to Scheme 4 in its physical effect.

We shall now describe some of the most striking phenomena encountered in vulcanization and oxidation, and attempt to give a plausible explanation for them based on Table 1 and on some working hypotheses which will be set up. The writer realizes that these working hypotheses are far from established and complete in all details.

WORKING HYPOTHESES

The possibility may be considered that the rubber molecules in the latex globules in the tree have the form of free-lying chain molecules, although the writer believes that this has by no means been proved. It is equally conceivable to him that molecular nets are present in the latex globule.

However, immediately the latex has left the tree for any time (perhaps even while it is still in the tree), nets which may have been formed according to Scheme 5, Table 1[32], are presumed to be present. The action of light or heat in the absence of oxygen promotes this cyclization. The action of oxygen under the influence of very definite oxidants leads to bridging, according to Scheme 4, possibly Scheme 3 or 5.

In such factory operations such as plasticizing and heating in the presence of oxygen, the molecule is easily broken off, as in Scheme 1a, Table 1. If no oxygen is present, the degradation effect (Scheme 2) of plasticization is very slight. If the action of light takes place in the presence of oxygen, then oxygen depolymerization predominates over the enlargement of the molecules by net-formation, as mentioned above. It is even probable that light and oxygen together have a more pronounced depolymerizing effect than oxygen alone; perhaps oxygen in its depolymerizing action is more powerfully activated by light than the double-bond in its cyclizing action.

In contrast to oxygen, sulfur always has the effect of enlarging molecules. Under the heading "Reduction in Tensile Strength Accompanying Overvulcanization", however, the possibility will be suggested that, after the stage of overvulcanization is reached, sulfur may have a depolymerizing effect.

TESTING THESE WORKING HYPOTHESES

It will be attempted to prove these working hypotheses against data from the literature.

Presence of chains in latex.—There are references[33] which indicate that plantation rubber is not completely soluble. Nevertheless, it is possible that at first there were chiefly loose chains present in the latex globules, and the insoluble part must perhaps be accounted for by the proteins or other impurities. But it is equally possible that there were net structures not completely severed during the washing process on the estates—which is also a kind of plasticization—aided by oxygen. For Spence and Ferry[34] have found in latex that was sterilized in sealed tins directly after tapping, up to almost 20 per cent of gel rubber, which their investigation shows was not formed as a result of sterilization. In commercial latex they found about 40 per cent gel rubber. We are, therefore, really still groping in the dark on the question as to whether nets were present in the latex when it was in the tree, and as long as the contrary is not proved, we shall keep this possibility open.

Formation of nets during storage.—It is a well-known phenomenon that[26] rubber in storage becomes more and more insoluble. From an investigation by Kemp and Peters[35] in particular, it appears that after latex films dry up, only a very small percentage of the rubber as a rule is soluble in organic solvents

such as benzene. It is only after dried rubber has been plasticized on the estate, by washing for instance, that a large part goes into solution. This end can be attained also by inducing the action of oxygen in other ways, *e.g.*, by warming thin sheets in the air or by exposure to sunlight in the presence of oxygen. Figure 7 illustrates this. On the basis of the argument given in connection with Equation (2), we may inquire whether the development of insolubility during storage is caused by net formation or by a linear growth of the chain molecules. In our opinion there is little room for doubt; the continued linear growth of the long-chain molecules at room temperature can scarcely be considered possible, if only on the ground that the chance of collision

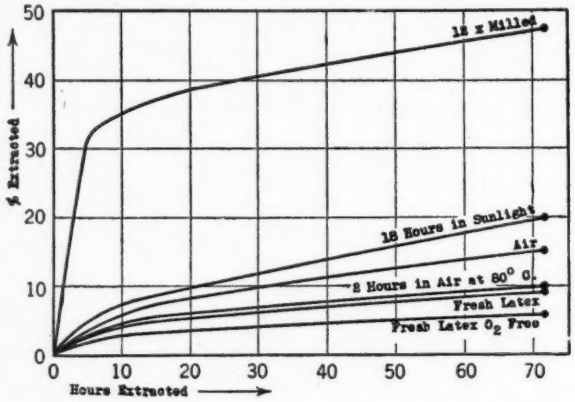


FIG. 7.—The soluble part of raw rubber can be increased by various kinds of treatment in the presence of oxygen.

between the two extremities is very slight. We shall, therefore, proceed from the thought that the insolubility of rubber is based on net formation, and in agreement herewith is the fact that crystals of gel rubber have elastic, and crystals of sol rubber, plastic properties; whereas after vulcanization (net formation), they show an equally elastic behavior[36].

The insoluble part, almost always present in natural rubber, has produced an overwhelming amount of investigation, especially in the earlier literature, and conflicting results have frequently been noted[37]. Sometimes we find that, when rubber is heated, the insoluble part increases; in other cases there is a decrease; occasionally there is first an increase, then a decrease. These contradictions are probably due largely to the fact that two opposing reactions take place simultaneously: oxygen depolymerization (Scheme 1), and polymerization by cyclization (Scheme 5, Table 1). This is clearly seen in an experiment by Garner[38] where irradiation in the presence of oxygen leads to a lowered viscosity, but in the absence of oxygen to gel formation (hence, increased viscosity). When it is considered that many investigators did not sufficiently realize the effect of slight traces of oxygen mentioned in the introductory paragraphs, or of the effect of light, it becomes plain that a lucid interpretation of the phenomena observed is difficult.

Apparently we may also assume that net formation due to oxygen takes place under the influence of certain oxidation agents, as benzoyl peroxide and nitrobenzene. Spence and Ferry[24] describe such an "oxygen vulcanization", among others, for naphthoquinone, *p*-benzoquinone, and potassium ferricy-

anide, provided no great excess of oxygen is present[39]; otherwise the depolymerizing action of oxygen (Scheme 1 ?) again predominates, as Table 3 shows.

TABLE 3

POLYMERIZATION AND DEPOLYMERIZATION BY OXYGEN UNDER THE INFLUENCE OF POTASSIUM FERRICYANIDE

$K_3Fe(CN)_6$ (per cent)	Treatment	Soluble in 14 days	Swelling index
0	untreated	75%	120
0	5 hrs. 100°, air absent	73%	110
0.3	5 hrs. 100°, air absent	22%	26
0	5 hrs. 100°, air present	92%	soluble
0.3	5 hrs. 100°, air present	89%	soluble

In Figure 8[34] it is shown that, in the presence of 1.2 per cent 1,4-naphthoquinone, the swelling and solubility of a rubber film decrease when irradiated, whereas the tensile strength increases very markedly. The ultimate value

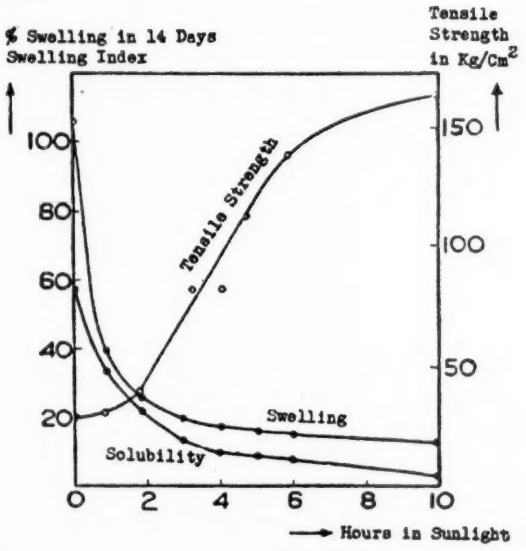
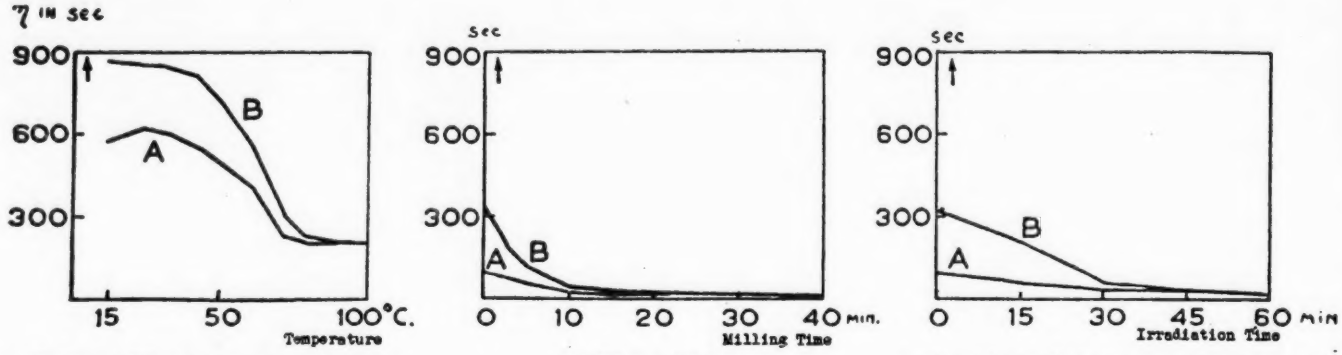


FIG. 8.—Polymerization by oxygen under the influence of oxidants (naphthoquinone).

obtained for tensile strength, about 140 kg. per sq. cm., is very reasonable in contrast to that of vulcanized rubber, which may be about 300 kg. per sq. cm. for sheet[40].

Depolymerization of rubber molecules by oxygen.—To show how the viscosity in solution is influenced by heating, plasticizing, and irradiation, in the presence of oxygen, we refer to Figure 9. In all these cases a decrease to the same final value is observed, indicating the formation of similar end products. Special attention is called to Figure 9c, which shows that irradiation in the presence of oxygen leads to depolymerization[41]. In these experiments, the contrast between oxygen and sulfur is clearly disclosed; thus addition of sulfur to the solution led to gelatinization after as little as 10–15 minutes of irradiation, and after 40 minutes 2.56 per cent of chemically combined sulfur was present.



a. Heating at different temperatures (five hours at 20° C; five hours at 30° C, etc.).

b. Milling at 80° C.

c. Ultraviolet irradiation at room temperature (very probably in presence of oxygen).

FIG. 9.—Decrease of the viscosity in solution by various kinds of treatment in presence of oxygen. The viscosity is measured by giving the flow period in seconds of a 3 per cent xylene solution. *A* is a Hevea plantation rubber, *B* a wild rubber.

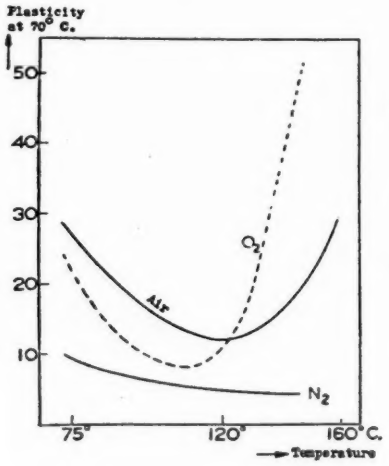


FIG. 10.—Influence on plasticity of temperature and various gases (plasticity measured in Goodrich plastometer).

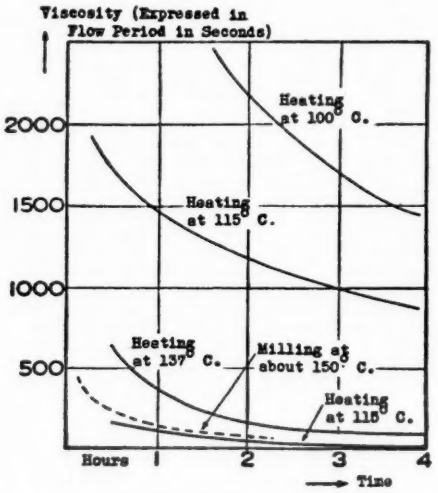


FIG. 11.—Effect of various degradation methods on the viscosity of rubber in solution.

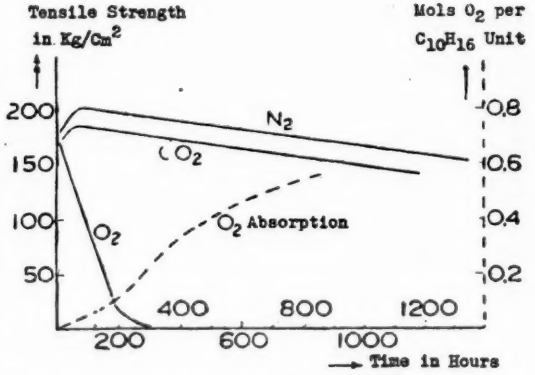


FIG. 12.—Connection between oxygen absorption and tensile strength.

It is interesting to review the comparison between heating and plasticization, because the belief is often met with in the rubber industry that plasticization actually amounts to a mechanical breaking up of the rubber molecules. This concept is probably only partly correct. The experiments by Busse and Cunningham[42], shown in Figure 10, teach that plasticizing in air at 75° C and 165° C, respectively, causes plasticity to increase four times as rapidly as at 120° C. It is likely that the molecules are more powerfully affected by mechanical influences at a lower temperature (75° C) because the rubber is stiffer. Apparently the combined action[43] of mechanical treatment and oxidation in this case leads to accelerated degradation because, as appears from Figure 10, this acceleration is not observed in an atmosphere of nitrogen. At a high temperature (165° C) this acceleration is obviously attributable to the increased rate of the oxygen reaction.

Reference may also be made to Figure 11, from Fry and Porritt[44], which indicates that milling at about 150° C has practically the same effect on viscosity in solution as heating at a similar temperature in air. These considerations led to the production of so-called softened rubber on estates where thin sheets of rubber are subjected to an oxidation process; by this means a saving is effected in the milling energy required for subsequent processing in the factory.

To what extent oxygen decreases the tensile strength of rubber[27] may be seen from Figure 12; 0.5 per cent oxygen (0.02 mol. O_2 per $C_{10}H_{16}$ unit) is sufficient[45] to reduce it by one-half. When heating takes place in inert gases, the tensile strength declines but little.

That the double bond—either directly or indirectly on the basis of Schmidt's rule—plays a great part in this breakdown of the chain is demonstrated by comparison with polybutene. Even ozone seems to have hardly any effect[14] on the latter, and if Figure 1 is compared with Figure 13, it is obvious that the absence of the double bond must be held responsible.

The conclusion is reached that oxygen may have a polymerizing as well as a depolymerizing action, and Spence and Ferry's study demonstrates that both reactions seem to proceed simultaneously. They have shown that the polymerizing reaction predominates when the rubber content is high; but when the rubber content is low, the depolymerizing reaction prevails. This is in complete agreement with expectations for when the rubber content is reduced, the chances of collision according to Schemes 3, 4, and 5 decrease, whereas those in accordance with Scheme 1 remain the same because the quantity of dissolved oxygen does not change. It may be assumed that the polymerizing reaction is one with low activation energy (light of 2500 A.U.), the depolymerizing reaction, one with high activation energy.

Tackiness is probably due to a breakdown of the molecule, coupled with the formation of dipoles (Scheme 1) but we shall not enter into details here. The phenomena observed for unvulcanized rubber differ in part from those for vulcanized rubber. For the latter material, Kohman[27] found:

with 0.02–0.05 mol O_2 per $C_{10}H_{16}$ group (0.5–1.25 weight % O_2) the rubber became tacky

with 0.5 mol O_2 per $C_{10}H_{16}$ group (12 weight % O_2) tackiness disappeared

with 1.0 mol O_2 per $C_{10}H_{16}$ group (24 weight % O_2) the rubber became brittle.

Accordingly it is sometimes observed that oxidation causes vulcanized rubber first to become softer, then harder, as the following data[46] show:

Shore durometer hardness after six hours at 100° C	35 units
Shore durometer hardness after three days at 100° C	27 units
Shore durometer hardness after two weeks at 100° C	15 units
Shore durometer hardness after four weeks at 100° C	25 units

These observations point to an initial depolymerization (Scheme 1?), followed by resinification (Scheme 4?); however, an exact interpretation is not yet possible.

Polymerizing effect of sulfur.—That sulfur during vulcanization leads to one or more of the possibilities for net formation indicated in Figure 4 is hardly open to doubt any longer. Confirmation of this is seen in the fact that polybutene which, as Figure 13 shows, contains no double bonds, cannot be vulcanized[14].

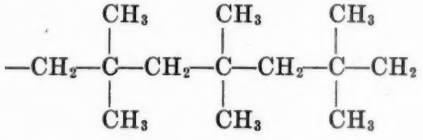


FIG. 13.—Polybutene.

On the other hand, the heat employed during vulcanization causes a slight amount of molecular degradation, which finds expression in a reduction of the tensile strength.

We shall now follow the changes in tensile strength as sulfur combination increases, shown in Figure 6[25].

The considerations under "Factors Which Play a Part in Oxidation" would seem to justify the expectation that progressively more intensive net formation would be accompanied by a continuous rise in tensile strength[47]; but this by no means proves to be the case. In Figure 6 we see that the tensile strength of raw rubber declines when plasticized, but rises again as soon as sulfur combination commences. All this is easy to understand; but now the important question arises: Why does the tensile strength begin to decrease after the combined sulfur exceeds 6 per cent and rise again at the so-called ebonite-forming stage? This will be discussed below.

SOME FURTHER CONSIDERATIONS ELICITED BY THE OXIDATION PROBLEM

Calculation of the molecular weight from viscosity measurements.—If the conclusions arrived at above on the simultaneous polymerization and depolymerization of rubber during storage and by oxidation are accepted, then sol rubber must not be regarded as a dispersion in which only individual chain molecules are present, but as one in which net fragments (hence three-dimensional substances) are also—perhaps predominantly—present. On this basis we shall suppose the structure of raw rubber to be as shown in Figure 3.

Kemp and Peters[48] have determined the molecular weight of various sol fractions by Staudinger's method. It was found that there is a continuous transition from sol to gel; the fraction having a molecular weight of 210,000 was designated as almost insoluble (hence the beginning of gel). If it is further considered that examination showed the gel to be 2000 per cent swollen, and

if the reasonable assumption is made that the net fragments of the sol rubber are also swollen to this degree, then, by calculation, a particle (if for the sake of convenience it is supposed to be a cube) with a molecular weight of 210,000, has a side of 200 A.U. Meyer and Jeannerat[49] have found that sol rubber just manages to pass through a filter with pores of 1000 A.U., which therefore indicates for sol rubber a size of the same order as that just determined. This agreement offers support for the concept of a three-dimensional structure of the net fragments. Measurements with an ultracentrifuge[9] also seem to lead to the conclusion that the rubber molecules in solution do not form stretched chains; it is assumed that the chains are rolled up or branched. From a hydrodynamic point of view, this amounts to the same as our assumption of net fragments.

Consequently if we proceed from the point that three-dimensional, loosely constructed particles (net fragments) are nearly always in large measure present in sol rubber, then the very important question immediately arises as to how far the Staudinger viscosity formula (1), which is based on the assumption that the molecules are long chains, retains its value[50].

Starting from the hypothesis that rubber molecules in solution may take the form of loose, easily deformable coils or clews, Kuhn[51], on the basis of hydrodynamic considerations, calculated that the following equation applies to such a coil:

$$\eta_{sp} = KcM^{0.8 \text{ to } 0.9} \qquad (4)$$

The writer[52] is of the opinion that a similar formula, but with a value of 0.6 for the exponent, may be developed from measurements by Staudinger, at least in the case of polar polyesters. In Table 4 the maximal ratios between

TABLE 4

MAXIMAL RATIO BETWEEN OSMOTICALLY AND VISCOSIMETRICALLY DETERMINED MOLECULAR WEIGHTS OF SOME POLYESTERS

Ester	Average mol. wt.		Ratio
	Osmotic	Viscosimetric	$\frac{\text{M. W. Osm.}}{\text{M. W. Visc.}}$
Polyvinyl acetate in acetone	330,000	40,000	8
Polyvinyl alcohol in water	78,000	21,000	3.7
Polyacrylic acid-methyl ester in acetone	321,000	30,000	6.5
Polymethacrylic acid-methyl ester in acetone	250,000	60,000	4.2

osmotically (actual) and viscosimetrically obtained molecular weights, as found by Staudinger and Warth[53], are given:

From Table 4 it may be concluded that the viscosimetric method gives a result for these polyesters which is three to eight times too low. However, the situation is probably less unfavorable in the case of rubber. For if loose, easily deformable, net fragments are assumed to be present[54], then from a hydrodynamic standpoint the same considerations as apply for Kuhn's coils or clews will also be valid here. But the rubber molecule is not polar; consequently the net fragments may be expected to be less closely packed than the polar polyester molecules; the exponent in (4) will therefore be higher than 0.6. It may even exceed 1, for Kuhn suggests a value of 2 as an extreme possibility.

Reduction in tensile strength accompanying overvulcanization.—Under "Polymerizing Effect of Sulfur" it was shown that when about 6 per cent of combined sulfur is exceeded (overvulcanization), the tensile strength suddenly declines

steeply. Heating alone cannot cause this decline, for when the sulfur content is low[55], the tensile strength scarcely decreases even when vulcanization is continued for eight hours—if a suitable accelerator is used.

The thought that oxidation phenomena play an important part in vulcanization is evoked by Figure 14, from Dufraisse and Etienne[56] which shows that oxidizability increases with the degree of vulcanization and is very considerable in precisely that interesting zone between 5 and 10 per cent combined sulfur, as Figure 6 indicates. Unfortunately Dufraisse's investigations do not go beyond mixes with 10 per cent combined sulfur; further work is therefore urgently needed here[57].

The question arises whether the oxidation taking place during vulcanization in the press, when about 6 per cent sulfur is combined, is sufficiently intensive to cause nets already formed to separate into fragments. To make this possible, at least two conditions must be satisfied:

(1) The rate of oxidation must be sufficiently great to start the depolymerization process in about one hour to two hours at 140° C (curing conditions).

(2) Enough oxygen must be present to reduce the tensile strength of about 1500 kg. per sq. cm. to 50 kg. per sq. cm.

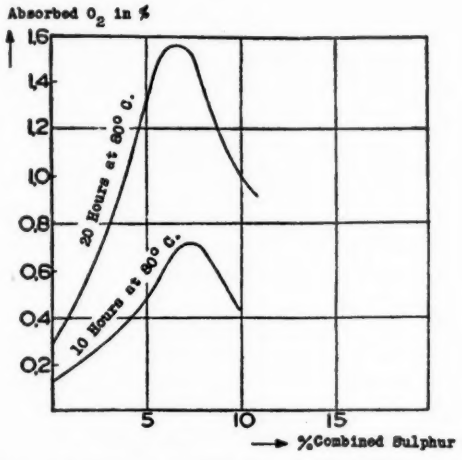


FIG. 14.—Connection between oxidizability and combined sulfur content. Oxidizability is expressed in percentage oxygen absorbed when heat is applied for one hour at 80° C, according to the Dufraisse method.

It should be noted that the investigation by Kemp and his collaborators[58] indicates that absorption of about 1.5 per cent oxygen is required to reduce the tensile strength to around 50 kg. per sq. cm.[59]. From the investigation by Kemp and associates[60], it can be deduced by extrapolation that in a mix with a maximum of 3 per cent combined sulfur, the rubber actually will absorb about 1.5 per cent oxygen in two hours at 140° C. If it is taken into account that the rate of oxidation increases with extraordinary rapidity as vulcanization progresses[61] (see Figure 14), then it is certain that, under the curing conditions in the press, the rate of oxidation is amply sufficient to reduce the tensile strength to 50 kg. per sq. cm.

As to the question whether enough oxygen is present in suitable form, we cannot speak with similar assurance, Williams and Neal[62] find that at 20° C,

only 0.02 per cent oxygen dissolves in rubber, and from data by Venable and Fuwa[63], it can be deduced by extrapolation that the solubility at 140° C would amount to only 0.004 per cent. But even if we consider the most favorable case, namely that oxygen has no opportunity to diffuse away during vulcanization, then 0.02 per cent still is insufficient, and the question arises whether oxygen is perhaps also present in a different form than the physically dissolved oxygen here discussed. Midgley and his collaborators[64] found that about 0.03 per cent oxygen is present as OH in natural rubber, but even if this is included, we are still a long way from the required 1.5 per cent.

Cramer and associates[65] found about 1.3 per cent oxygen in raw rubber, of which, however, approximately 1.2 per cent is present in the impure rubber hydrocarbons (resins, etc.). To what extent this 1.2 per cent is still active for further oxidation purposes must be considered. According to Cramer, when plasticizing is continued for 60 minutes, the oxygen content increases by 0.17 per cent and remains essentially constant during vulcanization. Ingredients like ZnO, S, etc., together contain only about 0.1 per cent oxygen, calculated on the rubber. This once more brings us to the conclusion that if the oxygen present in the impurities (in this case 1.2 per cent) is incapable of participating in the oxidation process, there is not enough oxygen present to explain the decline in the tensile strength which accompanies overvulcanization.

An investigation by van Rossem and Dekker[66] also points in the same direction; in rubber in an advanced state of cure (6.7 per cent combined sulfur), they found only 0.5 per cent oxidation product which contains about 0.02 per cent oxygen, calculated on the rubber. This figure agrees very well with the amount of oxygen physically dissolved in rubber, referred to above.

We come to the conclusion, therefore, that there is probably not enough oxygen present during vulcanization to explain the decline in tensile strength by oxidation, unless it is admitted that: (1) in rubber mixes with high sulfur content, the oxidation products which develop according to Scheme 1a or 1b in Table 1 again split off oxygen and are capable of renewed activity in breaking down the molecules; or (2) the oxygen present in the nonrubber components is capable of an oxidizing action. At present no sound arguments can be adduced in favor of either of these assumptions[67], and so we arrive at the question whether perhaps sulfur itself, when present in great excess, is capable of breaking down the molecules. It has been seen that, depending on the conditions, oxygen is capable of either a polymerizing or a depolymerizing action. Why should this not also be the case for the closely related element sulfur?

We do not wish now to enter into this possibility more deeply because still fewer quantitative data are available on this problem than exist on the oxidation problem itself. If there actually should be such a possibility, then working hypothesis No. 5 will have to be amplified. "In contrast to oxygen, sulfur always has the effect of enlarging molecules".

In a following article we hope to consider the mechanism of the oxidation reaction in rubber.

SUMMARY

After the structure of raw and vulcanized rubber is discussed, the reactions which probably take place between the rubber molecule, oxygen and sulfur, in presence and absence of light, are indicated. Depending on circumstances, a severance of the molecule or net formation may be expected (dehydrogenation, formation of oxygen and sulfur bridges, cyclization); see Table 1.

The accompanying changes in solubility, viscosity in solution, tensile strength, hardness and tackiness, are described.

Special attention is drawn to the great effect that traces of oxygen, so slight that they cannot be shown analytically, may have because of the highly polymerized structure of rubber.

Working hypotheses are established to explain the effect of the external factors mentioned, and these hypotheses are tested against extensive observation material. One of the most important conclusions is that it must probably be assumed that net-formed (chiefly cyclized) aggregates are present in unvulcanized rubber instead of, or in addition to, chain molecules (Figure 3). How this affects the value of the method of determining molecular weight from viscosity measurements is discussed, and it is suggested that Kuhn's viscosity formula (4), probably with modification of the value of the exponent, will have to be applied instead of the Staudinger formula (1).

It is also attempted to explain the drop in tensile strength to about 50 kg. per sq. cm. (see Figure 6) which occurs after optimum vulcanization is exceeded. It is attempted to place the responsibility for this on the oxidation which takes place during vulcanization. But it is shown by calculation that the conditions for this are in all probability not fulfilled. The rate of oxidation is high enough to reduce the tensile strength to 50 kg. per sq. cm. during normal curing conditions, but the amount of oxygen required for this purpose, about 1.5 per cent, is probably not present in rubber in a suitable form. A conclusive explanation of this decrease in tensile cannot as yet be given.

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[30] Since $2l$ passes over into l, and the thickness d does not appear in Equation (1), a decrease in n is to be expected.
[31] The double bond actually does play a preponderant part here. An argument in favor of the cyclization theory appears from the fact that hydrorubber, polystyrene (cf. *Kautschuk*, Nov. **1934**) and polybutene[14] are not converted into insoluble products by irradiation.
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[59] The investigation by Kohman (*J. Phys. Chem.* **33**, 226 (1928)) teaches us approximately the same thing. In this calculation, σ_{max}, calculated on the actual average is taken into consideration (cf. note 29).
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RESILIENT ENERGY *

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Wiegand[1] introduced the term "resilient energy" or "proof resilience", and considered it to be a measure of the reinforcement of vulcanized rubber. The resilient energy is obtained by measuring the area between the stress-strain curve and the elongation axis, or, to express this energy in another manner, the stress is integrated with respect to the elongation, the limits being the elongation at the breaking stress and zero. The integration of stress with respect to elongation could be performed accurately if stress could be expressed in terms of elongation.

The rubber scientist has investigated the stress-strain relationship of rubber chiefly with the object of extending knowledge of the structure of rubber, whereas the rubber technologist uses the stress-strain curves between the elongation at the breaking stress and at zero to enable him to evaluate the qualities of his compounds. A method for relating stress to strain for vulcanized rubber would benefit the rubber technologist in evaluating the reinforcing qualities of his pigments or fillers. Several formulas[2] exist, but, in general, they cannot easily be applied to the data obtained for stress and elongation on machines adapted to testing the tensile strength of vulcanized rubber.

Recently, Mark[3] has stated that the elastic behavior of stressed rubber can be divided into three elementary processes; taken in order, they are, first, an unfolding and unrolling of interlocked and entangled chain molecules; secondly, a process of crystallization of the rubber while under stress, the amorphous and crystalline forms being in equilibrium; and, thirdly, the rubber being now largely crystalline, its extension as a crystalline substance. Mark pointed out that the processes may overlap; they depend on experimental conditions, and are intricate and complicated.

The theory and method of calculation of the resilient energy.—In this communication, the theory and the method of the calculations are first evolved and then illustrated by practical work on a series of compounds containing various proportions of a reinforcing agent. For the practical work, the tensile strengths of samples of vulcanized rubber containing various proportions of filler and cured for different periods were obtained and, by means of the calculus of finite differences, expressed in terms of their elongations; these expressions having been obtained, they were integrated with respect to the elongations and the resilient energy of each sample calculated. A method of dividing the resilient energy into the partial resilient energies of the filler and of the base mix was proposed and illustrated by graphs (Figures 1 and 2).

No success was obtained when the tensile strength was based on the original cross-sectional area of the test-piece, but a solution was possible when the stress was calculated on the theoretical cross-sectional area, vacuoles being neglected, although it was recognized that this neglect might introduce an error.

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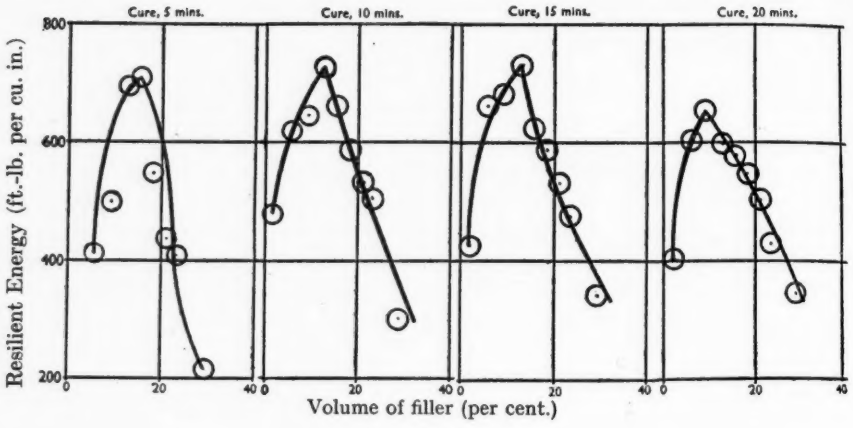

FIG. 1.

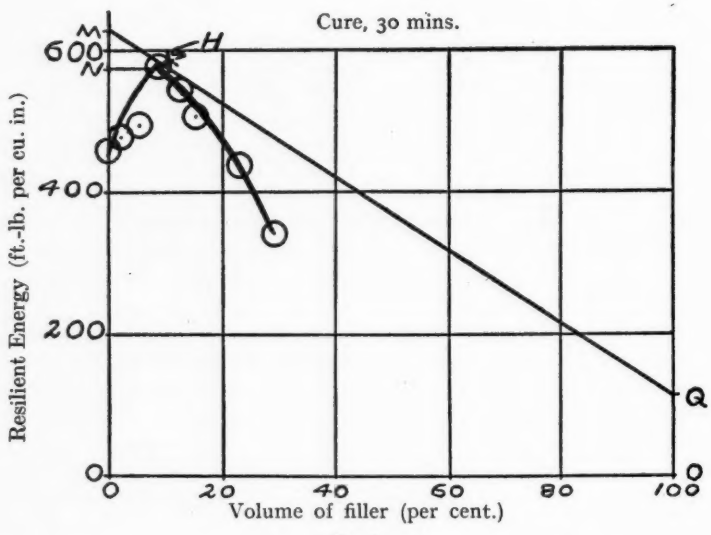

FIG. 2.

Let T = stress based on the original cross-sectional area (lbs. per sq. in.)

Let E = elongation (inches per inch length of test-piece)

suffix b = value of T and of E at the breaking point of the test-piece

$\therefore$ $T(E+1)$ = stress based on the theoretical cross-sectional area (lbs. per sq. in.)

If $T(E+1)$ = a function of $E = f(E)$

the resilient energy $= \int_0^{Eb} T\,dE = \int_0^{Eb} f(E)\,\frac{1}{E+1}\,dE$ inch-pounds per cu. in.

$$= \frac{1}{12}\int_0^{Eb} f(E)\,\frac{1}{E+1}\,dE \text{ ft.-lb. per cu. in.} \qquad (1)$$

The resilient energy is thus calculated on the value of T, based on the original, not on the theoretical cross-sectional area. Intermediate limits may be substituted for E_b and $E = 0$, followed by addition of the separate functions to give the total resilient energy.

Values of T, obtained from the graph given by the Scott tensile-testing machine, were multiplied by $(E + 1)$ to give $T(E + 1)$. A graph of $T(E + 1)$ against E was obtained, and values of $T(E + 1)$ for every value of $E = 0.5$ were read off from the graph and were used in a table of differences.

A table of differences has the general form[4]:

Argument	Entry	Δ	Δ^2	Δ^3
a	$f(a)$			
$a + w$	$f(a + w)$	$\Delta f(a)$	$\Delta^2 f(a)$	
$a + 2w$	$f(a + 2w)$	$\Delta f(a + w)$	$\Delta^2 f(a + w)$	$\Delta^3 f(a)$
$a + 3w$	$f(a + 3w)$	$\Delta f(a + 2w)$	$\Delta^2 f(a + 2w)$	$\Delta^3 f(a + w)$
$a + 4w$	$f(a + 4w)$	$\Delta f(a + 3w)$	$\Delta^2 f(a + 3w)$	$\Delta^3 f(a + 2w)$

Let y = a function of an argument $u = f(u)$
and $u = a + xw$,
then a, $a + w$, etc. = values of the argument u
$f(a)$, $f(a + w)$, etc. = the values of y corresponding to a, $a + w$, etc., respectively
$\Delta f(a)$, $\Delta^2 f(a)$, $\Delta^3 f(a)$ = the first, second, third, etc., differences in the values of y corresponding to the respective values of the argument
Δ, Δ^2, Δ^3, etc., denote the first, second, third, etc., order of differences.

This table of differences is continued until the differences of the nth order are constant, then:

$$y = f(a) + x\Delta f(a) + \frac{x(x-1)}{2!}\Delta^2 f(a) + \frac{x(x-1)(x-2)}{3!}\Delta^3 f(a) + \cdots + \frac{x(x-1)\cdots(x-n+1)}{n!}\Delta^2 f(a) \quad (2)$$

which is the Gregory-Newton formula of interpolation.

Any continuous function will give a constant value for a certain order of differences. Values for the differences can be substituted in Equation (2) which will have the form of a polynomial, a form of equation which is integrated easily:

$$\int y dx = f(a)\int dx + \Delta f(a)\int x dx + \frac{\Delta^2 f(a)}{2!}\int x(x-1)dx + \frac{\Delta^3 f(a)}{3!}\int x(x-1)(x-2)dx + \cdots + \frac{\Delta^n f(a)}{n!}\int x(x-1)\cdots(x-n+1)dx \quad (3)$$

which is the Newton-Cotes integration formula. In this instance the integration of the formula for the tensile strength, $f(E)\,\frac{1}{E+1}$, gives the resilient energy.

Partial resilient energy of base mix and of filler.—The idea of partial resilient energies of rubber and of filler was proposed by Lunn[5]. As certain ingredients are necessary for the vulcanization of rubber, the compound may be divided into rubber plus vulcanizing ingredients as the base mix and the reinforcing agent or filler.

The first stage in the separation of the resilient energy into its partial quantities is the plotting of the resilient energy as ordinates and the amount of filler, 0 to 100 per cent, as abscissae.

Let R, R_B and R_F be the resilient energies (ft.-lb. per cu. in.) of the compound, base mix, and filler, respectively.

Let N_B and N_F = volume fractions of base mix and of filler, respectively
then $R = N_B R_B + N_F R_F$ (4)

In a compound, base mix plus filler, the partial resilient energies per unit volume of base mix and of filler either remain constant, whatever the proportions, or vary according to the proportions of filler. In the first class of compounds the base mix and filler behave as a mechanical mixture; in the second class as a mixture in which base mix and filler mutually affect one another.

For compounds of the second class, the variation of the partial resilient energies, R_B and R_F, with composition may be found according to the methods of Lewis and Randall[6]; their method of tangent intercepts is presented by Hougen and Watson[7], and is illustrated in Figure 2, in which the resilient energy of the compound is plotted against the composition by volume. A tangent to this curve is drawn at any desired concentration of filler; the intersection of the tangent with the ordinate for 0 per cent filler gives the partial resilient energy of the base mix and, similarly, the intersection with the ordinate for a 100 per cent filler gives the partial resilient energy of the filler.

The proof of the method of tangent intercepts, adapted from the proof given by Hougen and Watson, is:

Let A = total resilient energy of a compound containing v_B cubic inches of base mix and v_F cubic inches of filler.

Let R, R_B, R_F, N_B and N_F represent the same quantities as in Equation (4) above.

Hence

$$R = \frac{A}{v_B + v_F} \tag{5}$$

and

$$N_F = \frac{v_F}{v_B + v_F} \tag{6}$$

In Figure 2 the slope of the tangent at any point H is equal to $\frac{dR}{dN_F}$ and also:

$$OM = ON + MN = R - N_F \frac{dR}{dN_F} \tag{7}$$

The volume fraction of the filler may be varied by addition or removal of the base mix, thus v_F remains constant, and

$$\left(\frac{\delta A}{\delta v_B}\right)_{v_F} = R_B \tag{8}$$

When v_F is treated as a constant and Equation (5) is differentiated with re-

spect to v_B:

$$dR = \frac{dA}{v_B + v_F} - \frac{A dv_B}{(v_B + v_F)^2}. \tag{9}$$

Differentiating Equation (6) with respect to v_B and keeping v_F constant:

$$dN_F = \frac{-v_F \cdot dv_B}{(v_B + v_F)^2}. \tag{10}$$

Combining Equations (9) and (10):

$$\frac{dR}{dN_F} = \frac{-dA(v_B + v_F)}{v_F \cdot dv_B} + \frac{A}{v_F}. \tag{11}$$

Substituting Equation (11) in Equation (7):

$$OM = R + \frac{N_F dA(v_B + v_F)}{v_F dv_B} - \frac{N_F A}{v_F} \tag{12}$$

Substituting Equations (5) and (6) in Equation (12):

$$OM = R + \frac{dA}{dv_B} - R = \frac{dA}{dv_B}.$$

As v_F was treated as constant in all the differentiations:

$$\frac{dA}{dv_B} = \left(\frac{\delta A}{\delta v_B}\right)_{v_F}$$

and, from Equation (8):

$$OM = R_B.$$

Similarly, by treating v_B as a constant:

$$OQ = R_F.$$

Thus, the partial resilient energies of the base mix and of the filler may be found by measurement of intercepts given by the intersections of the tangent with the ordinates for zero and 100 per cent filler, the tangent being drawn at any point corresponding to a volume percentage of filler.

RESULTS

The following compounds were mixed on a laboratory mill having 12 in. × 6 in. rolls, were left for at least 24 hours, and then were vulcanized in a press.

TABLE 1

Base mix	Parts by weight	Parts by volume
Pale crepe rubber	100	108.7
Zinc oxide	5	0.90
Sulfur	2.5	1.22
Benzothiazyl disulfide	1	0.67
Tetramethylthiuram disulfide	0.1	0.08
	108.6	111.57

FILLER—REINFORCING AGENT

Light magnesium carbonate (Parts per 100 parts by weight of rubber)		Composition of compound (Per cent by volume)	
By weight	By volume	Base mix	Filler
5	2.25	98.02	1.98
15	6.75	94.30	5.70
25	11.25	90.83	9.17
35	15.75	87.62	12.38
45	20.25	84.48	15.52
55	24.75	81.85	18.15
65	29.25	79.20	20.80
75	33.75	76.8	23.2
100	45.00	71.3	28.7

The compounds were vulcanized at 20 lbs. gauge steam pressure for 5, 10, 15, 20 and 30 minutes in the form of sheets approximately 0.100 inch thick.

The sheets of vulcanized compound were allowed to stand for 24 hours, dumb-bell test-pieces stamped out from the sheets, and the pieces pulled on the Scott tensile testing machine at room temperature at a rate of 20 inches per minute. The tensile strength was measured for every 100 per cent elongation of the test-piece, the original marks being 1 inch apart. The tensile strengths, expressed on the original cross-sectional area, were read off the standard sheets supplied with the Scott machine, multiplied by the factor $(E + 1)$ to convert them to a tensile strength based on the theoretical cross-sectional area, and the new tensile results plotted against the elongation. A smooth curve was drawn through the points and the tensile strength read off from the curve at intervals of 50 per cent elongation. An example illustrating the procedure is given. A table of differences was constructed for every sample of the vulcanized compounds, each difference being placed between and to the right of the entries or differences to which it related.

It may be noted here that the above mentioned compounds were not designed, vulcanized or tested for tensile strength for this series of tests on resilient energy, but, because of the present emergency, practical work for such tests could not be done. However, it was decided to test this method for the calculation of resilient energy on a series of results which were at hand rather than proceed with the work at a later date.

Tables of differences for tensile strengths.—The compounds are placed in order of ascending magnesium carbonate by volume and of ascending periods of cure (the tables are headed by the carbonate of magnesia content and time of cure).

In many of the tables the three processes mentioned by Mark[3] were made noticeable by the fact that the table consists of three functions which give three sets of differences; these sets of differences are divided from one another by dotted lines. Some tables appear to consist of two sets and others, especially heavily loaded compounds, of one set of differences.

Two examples of the difference tables are given, the tensile strengths of all other cures being treated in a manner similar to the examples.

0 per cent/5′, 1.98 per cent/5′, 0 per cent/10′, 0 per cent/15′ and 0 per cent/20′—no cure. The cures for which tables of differences were tabulated are: 5.70 per cent, 9.17 per cent, 12.38 per cent, 15.52 per cent, 18.15 per cent, 20.8 per cent, 23.2 per cent and 28.7 per cent at 5, 10, 15, 20 and 30 minutes;

1.98 per cent at 10, 15, 20 and 30 minutes; the exceptions are 30-minute cures for 18.15 per cent and 20.8 per cent.

5.70 per cent/5′ Elongation at break = 7.2 inches per inch

Argument E	Entry $T(E+1)$	Δ	Δ^2	Δ^3	Δ^4
0	0				
		25			
0·5	25		40		
		65		10	
1·0	90		50		
		115		10	
1·5	205		60		
		175		−10	
2·0	380		50		
		225		30	
2·5	605		80		30
		305		60	
3·0	910		140		50
		445		110	
3·5	1355		250		55
		695		165	
4·0	2050		415		40
		1110		205	
4·5	3160		620		25
		1730		230	
5·0	4890		850		50
		2580		280	
5·5	7470		1130		30
		3710		310	
6·0	11180		1440		20
		5150		330	
6·5	16330		1770		
		6920			
7·0	23250				
		6870			
7·5	30120				

Function 1. $E = 0$ –2.0, Δ^3 = constant = 10
" 2. $E = 2.0$–7.0, Δ^4 = constant, average = 40
" 3. $E = 7.0$–7.5, Δ = constant = 6870

28.7 per cent/30′ Elongation at break = 3.6 inches per inch

E	$T(E+1)$	Δ	Δ^2
0	0		
		430	
0.5	430		280
		710	
1.0	1140		350
		1060	
1.5	2200		340
		1400	
2.0	3600		360
		1760	
2.5	5360		360
		2120	
3.0	7480		340
		2460	
3.5	9940		

Function 1. $E = 0$–3.5, Δ^2 = constant, average = 340

The following table gives an example of the method of compiling the difference table from the tensile strength as given by the original graph from the Scott machine.

28.7 per cent/30′

E	$E+1$	T from original graph	$T(E+1)$ from original graph	$T(E+1)$ taken from curve of $T(E+1)$ *vs.* E
0	1	0	0	0
0.5	1.5	...	...	430
1.0	2.0	...	...	1140
1.5	2.5	...	...	2200
2.0	3.0	1200	3600	3600
2.5	3.5	...	...	5360
3.0	4.0	1865	7460	7480
3.5	4.5	...	...	9940
3.6	4.6	2205	10140	10140

Calculation of resilient energies.—An expression for the tensile strength of each sample was obtained from the above tables of differences by the use of Formula (2); this having been obtained, it was substituted as $f(E)$ in Equation (1), which was expanded into Equation (3) to give the resilient energy. When the difference table for a sample has been divided into sets of differences, the function corresponding to each set of differences was obtained and was integrated separately; the sum of these integrals gave the resilient energy for the sample.

The tensile strength based on the theoretical cross-sectional area takes the form of Equation (2), where $y = T(E+1)$ and $f(a)$, $\Delta f(a)$, $\Delta^2 f(a)$, etc., are the values taken from the above tables.

Beginning at the top of a table of differences, where $a = 0$ in the argument $u = a + xw$, and, as the intervals in the argument are 0.5 (*i.e.*, $w = \frac{1}{2}$), also $E = u$, then:

$$x = 2E.$$

Equation (2) then becomes:

$$T(E+1) = f(a) + \frac{2E}{1}\Delta f(a) + \frac{2E(2E-1)}{2.1}\Delta^2 f(a) \frac{2E(2E-1)(2E-2)}{3\cdot 2\cdot 1}\Delta^3 f(a) \frac{2E(2E-1)(2E-2)(2E-3)}{4\cdot 3\cdot 2\cdot 1}\Delta^4 f(a) \frac{2E(2E-1)(2E-2)(2E-3)(2E-4)}{5\cdot 4\cdot 3\cdot 2\cdot 1}\Delta^5 f(a). \quad (13)$$

Equation (13) is expanded into a polynomial, divided by $(E+1)$, and integrated to give the resilient energies of each first function of each difference table.

When the function begins at the point where, for example, $a = 2$, that is, at the fifth argument:

$$E = 2 + \tfrac{1}{2}x,$$

that is,

$$x = 2E - 4,$$

then $T(E+1) = f(a+4w) + (2E-4)\Delta f(a+4w)$

$$\frac{(2E-4)(2E-5)}{2\cdot 1}\Delta^2 f(a+4w) + \text{etc.} \qquad (13a)$$

Functions beginning at other values for the argument are treated similarly.

The calculation of the resilient energy of the sample 5.70 per cent/5′ is given in full as an example, after which the expressions for resilient energies are given in tabular form in Table 2. The values for the resilient energies were confirmed by the trapezoidal rule.

Calculation of resilient energy of the sample.—5.70 per cent/5′.

Function 1.—Tensile strength = $T(E+1)$, taken from difference Table 2. By Equation (13):

$$\begin{aligned} T(E+1) &= f(a) + 2E\Delta f(a) + \frac{2E^2-E}{1}\Delta^2 f(a) + \frac{4E^3-6E^2+2E}{3}\Delta^3 f(a) \\ &= 0 + 2E.25 + \frac{2E^2-E}{1}.40 + \frac{4E^3-6E^2+2E}{3}.10 \\ &= 50E + 80E^2 - 40E + \frac{40}{3}E^3 - \frac{60}{3}E^2 + \frac{20}{3}E \\ &= \frac{40}{3}E^3 + 60E^2 + \frac{50}{3}E + 0. \end{aligned}$$

Thus the coefficients of E in the expression for tensile strength tabulated in Table 2 are: $\frac{40}{3}$, 60, $\frac{50}{3}$, 0.

$$\begin{aligned} \text{Resilient energy} &= \frac{1}{12}\int_0^E f(E)\,\frac{1}{E+1}\,dE \qquad (1) \\ &= \frac{1}{12}\int_0^2 \left(\frac{40}{3}E^3 + 60E^2 + \frac{50}{3}E\right)\frac{1}{E+1}\,dE \\ &= \frac{1}{12}\int_0^2 \left(\frac{40}{3}E^2 + \frac{140}{3}E - 30 + \frac{30}{E+1}\right)dE \\ &= \frac{1}{12}\left[\frac{40}{9}E^3 + \frac{70}{3}E^2 - 30E + 30\log_e(E+1)\right]_0^2 \end{aligned}$$

Similarly, the coefficients of E tabulated in Table 2 under resilient energy are: $\frac{40}{9}$, $\frac{70}{3}$, -30, 30.

Substituting the upper and the lower limits of E in this last equation, the terms are:

$$\begin{aligned} \text{Resilient energy} &= \frac{1}{12}(35.5 + 93.3 - 60 + 33) \\ &= \frac{1}{12}(101.8) \end{aligned}$$

Function 2.—The values of $T(E+1)$ from 380 to 23250 are regarded as a table of differences separate from those of function 1.

$$T(E+1) = 380 + (2E-4)\,.225 + (2E^2 - 9E + 10)\,.80 + \frac{4E^3 - 30E^2 + 74E - 60}{3}\,.60 + \frac{4E^4 - 44E^3 + 179E^2 - 319E + 210}{6}\,.40$$

$$= 380 + 450E - 900 + 160E^2 - 720E + 800 + 80E^3 - 600E, + 1480E - 1200 + \frac{80}{3}E^4 - \frac{880}{3}E^3 + \frac{3580}{3}E^2 - \frac{6380}{3}E + 1400$$

$$= \frac{80}{3}E^4 - \frac{640}{3}E^3 + \frac{2260}{3}E^2 - \frac{2750}{3}E + 480$$

These coefficients of E are tabulated in Table 2 under 5.70 per cent/5′² function 2, tensile strength.

$$\text{Resilient energy} = \frac{1}{12}\int_2^7 \left(\frac{80}{3}E^4 - \frac{640}{3}E^3 + \frac{2260}{3}E^2 - \frac{2750}{3}E + 480\right)\frac{dE}{E+1}$$

$$= \frac{1}{12}\int_2^7 \left(\frac{80}{3}E^3 - 240\,E^2 + \frac{2980}{3}E - 1910 + \frac{2390}{E+1}\right)dE$$

$$= \frac{1}{12}\left[\frac{20}{3}E^4 - 80E^3 + \frac{1490}{3}E^2 - 1910E + 2390\log_e(E+1)\right]_2^7$$

$$= \frac{1}{12}[15900 - 26800 + 22350 - 9550 + 2344.1]$$

$$= \frac{1}{12}[4244.1]$$

Function 3.—$E = 7.0 - 7.5$. $E_b = 7.2$.

The argument $E = 7 + x\cdot\frac{1}{2}$

therefore $x = 2E - 14$.

$$T(E+1) = 23250 + (2E - 14).6870 = 13740E - 72930.$$

$$\text{Resilient energy} = \frac{1}{12}\int_{7.0}^{7.2}(13740E - 72930)\,\frac{1}{E+1}\,dE$$

$$= \frac{1}{12}\int_{7.0}^{7.2}\left(13740 - \frac{86670}{E+1}\right)dE$$

$$= \frac{1}{12}\left[13740E - 86670\log_e(E+1)\right]_{7.0}^{7.2}$$

$$= \frac{1}{12}[2748 - 2140]$$

$$= \frac{1}{12}[608]$$

TABLE 2

Sample	Function	Tensile strength, $T(E+1)$						Resilient energy						Limits of E		Resilient energy	
		Coefficients of:						Coefficients of:								Functional in.-lbs. per cu. in.	Total ft.-lbs. per cu. in.
		E^5	E^4	E^3	E^2	E	No.	E^5	E^4	E^3	E^2	E	$\text{Log}_e(E+1)$	Upper	Lower		
5.70%/5′	1	—	—	$\frac{40}{3}$	60	$\frac{50}{3}$	0	—		$\frac{40}{9}$	$\frac{70}{3}$	−30	30	2	0	101.8	
"	2	—	$\frac{80}{3}$	$-\frac{640}{3}$	$\frac{2260}{3}$	$-\frac{2750}{3}$	480	—	$\frac{20}{3}$	−80	$\frac{1490}{3}$	−1910	2390	7	2	4244.1	412.8
"	3	—	—	—	—	13740	−72930	—	—	—	—	13740	−86670	7.2	7	608.0	
9.17%/5′	1	—	—	20	30	100	0	—	—	$\frac{20}{3}$	5	90	−90	2	0	154.4	
"	2	—	30	−250	$\frac{1965}{2}$	$-\frac{2875}{2}$	955	—	$\frac{15}{2}$	$-\frac{280}{3}$	$\frac{2525}{4}$	−2700	3655	7	2	5112.1	492.2
"	3	—	—	—	—	16000	−87700	—	—	—	—	16000	−103700	7.2	7	639.4	
12.38%/5′	1	—	$\frac{40}{3}$	$-\frac{40}{3}$	$\frac{230}{3}$	$\frac{490}{3}$	0	—	$\frac{10}{3}$	$-\frac{80}{9}$	$\frac{155}{3}$	60	−60	5.5	0	3351.9	688.2
"	2	—	—	—	—	11614	−48647	—	—	—	—	11614	−60261	7.0	5.5	4907.0	
15.52%/5′	1	—	10	$\frac{70}{3}$	$\frac{135}{2}$	$\frac{1795}{6}$	0	—	$\frac{5}{2}$	$\frac{40}{9}$	$\frac{325}{12}$	245	−245	6	0	6168.2	709.5
"	2	—	—	—	—	10350	−41050	—	—	—	—	10350	−51400	6.7	6	2346.1	
18.15%/5′	1	—	$\frac{40}{3}$	0	$\frac{350}{3}$	380	0	—	$\frac{10}{3}$	$-\frac{40}{9}$	65	250	−250	5	0	3954.9	556.3
"	2	—	—	—	—	8140	−27020	—	—	—	—	8140	−35160	6.0	5	2720.2	
20.8%/5′	1	—	20	$-\frac{20}{3}$	135	$\frac{1175}{3}$	0	—	5	$-\frac{80}{9}$	$\frac{485}{6}$	230	−230	4	0	2544.2	436.0
"	2	—	—	—	—	6900	−19100	—	—	—	—	6900	−26000	5.2	4	2687.2	
23.2%/5′	1	—	—	80	200	320	0	—	—	$\frac{80}{3}$	60	200	−200	4.8	0	4939.9	411.7

TABLE 2—*continued*

Sample	Function	Tensile strength, $T(E+1)$						Resilient energy						Limits of E		Resilient energy	
		Coefficients of:						Coefficients of:								Functional in.-lbs. per cu. in.	Total ft.-lbs. per cu. in.
		E^5	E^4	E^3	E^2	E	No.	E^5	E^4	E^3	E^2	E	$\text{Log}_e(E+1)$	Upper	Lower		
28.7%/5′	1	—	—	60	310	270	0	—	—	20	125	20	−20	3.6	0	2594.6	216.2
1.98%/10′	1	—	—	20	30	40	0	—	—	$\frac{20}{3}$	5	30	−30	2	0	100.3	
"	2	$\frac{16}{3}$	−60	$\frac{860}{3}$	−535	573	−160	$\frac{16}{15}$	$-\frac{49}{3}$	$\frac{352}{3}$	$-\frac{887}{2}$	1460	−1620	7	2	3998.6	477.1
"	3	—	—	—	—	15300	−84050	—	—	—	—	15300	−99350	7.5	7	1626.5	
5.70%/10′	1	—	$\frac{10}{3}$	$-\frac{10}{3}$	$\frac{295}{6}$	$\frac{1655}{6}$	0	—	$\frac{5}{6}$	$-\frac{20}{9}$	$\frac{335}{12}$	220	−220	2	0	305.5	
"	2	$\frac{20}{3}$	$-\frac{250}{3}$	$\frac{1565}{3}$	$-\frac{9835}{6}$	$\frac{17995}{6}$	−1720	$\frac{4}{3}$	$-\frac{45}{2}$	$\frac{1835}{9}$	$-\frac{13505}{12}$	5250	−6970	6.5	2	4179.1	626.8
"	3	—	—	—	—	14950	−76975	—	—	—	—	14950	−91925	7.4	6.5	3037.0	
9.17%/10′	1	—	$\frac{20}{3}$	$\frac{20}{3}$	$\frac{85}{3}$	$\frac{550}{3}$	0	—	$\frac{5}{3}$	0	$\frac{85}{6}$	155	−155	6	0	3298.0	644.9
"	2	—	—	—	—	12010	−53575	—	—	—	—	12010	−65585	7.3	6	4441.0	
12.38%/10′	1	—	$\frac{40}{3}$	0	$\frac{290}{3}$	210	0	—	$\frac{10}{3}$	$-\frac{40}{9}$	55	100	−100	5.5	0	4337.4	730.7
"	2	—	—	—	—	10120	−39800	—	—	—	—	10120	−49920	6.9	5.5	4430.7	
15.52%/10′	1	—	$\frac{40}{3}$	$\frac{40}{3}$	$\frac{170}{3}$	$\frac{1090}{3}$	0	—	$\frac{10}{3}$	$\frac{40}{9}$	$\frac{65}{3}$	320	−320	5	0	4207.2	664.9
"	2	—	—	—	—	8860	−30640	—	—	—	—	8860	−39500	6.3	5	3771.6	
18.15%/10′	1	—	$\frac{20}{3}$	20	$\frac{295}{3}$	485	0	—	$\frac{5}{3}$	$\frac{40}{9}$	$\frac{85}{2}$	400	−400	5	0	3943.0	577.4
"	2	—	—	—	—	9730	−34020	—	—	—	—	9730	−43750	6.0	5	3986.0	

TABLE 2—*continued*

TABLE 2—*continued*

Sample	Function	Tensile strength, $T(E+1)$						Resilient energy						Limits of E		Resilient energy	
		Coefficients of:						Coefficients of:								Functional in.-lbs. per cu. in.	Total ft.-lbs. per cu. in.
		E^5	E^4	E^3	E^2	E	No.	E^5	E^4	E^3	E^2	E	$\text{Log}_e(E+1)$	Upper	Lower		
20.8%/10′	1	—	$\frac{40}{3}$	40	$\frac{230}{3}$	510	0	—	$\frac{10}{3}$	$\frac{80}{9}$	25	460	−460	4	0	2921.9	531.8
"	2	—	—	—	—	6880	−18120	—	—	—	—	6880	−25000	5.4	4	3460.2	
23.2%/10′	1	—	—	$\frac{160}{3}$	280	$\frac{1220}{3}$	0	—	—	$\frac{160}{9}$	$\frac{340}{3}$	180	−180	5.2	0	6171.8	514.3
28.7%/10′	1	—	—	40	460	440	0	—	—	$\frac{40}{3}$	210	20	−20	3.7	0	3953.3	299.4
1.98%/15′	1	—	—	$\frac{40}{3}$	60	$\frac{80}{3}$	0	—	—	$\frac{40}{9}$	$\frac{70}{3}$	−20	20	3	0	297.7	425.6
"	2	$\frac{8}{3}$	$-\frac{80}{3}$	$\frac{550}{3}$	$-\frac{2080}{3}$	1804	−1590	$\frac{8}{15}$	$-\frac{22}{3}$	$\frac{638}{9}$	−453	2710	−4300	7.3	3	4809.3	
5.70%/15′	1	—	—	$\frac{40}{3}$	60	$\frac{380}{3}$	0	—	—	$\frac{40}{9}$	$\frac{70}{3}$	80	−80	2	0	210.0	
"	2	$\frac{16}{3}$	−50	250	$-\frac{1195}{2}$	$\frac{6553}{6}$	−565	$\frac{16}{15}$	$-\frac{83}{6}$	$\frac{916}{9}$	$-\frac{5417}{12}$	1995	−2560	6	2	3089.2	662.4
"	3	—	—	—	170	10435	−53910	—	—	—	85	10265	−73985	7.5	6	4658.8	
9.17%/15′	1	—	—	$\frac{80}{3}$	40	$\frac{640}{3}$	0	—	—	$\frac{80}{9}$	$\frac{20}{3}$	200	−200	2	0	278.1	
"	2	—	10	50	$-\frac{625}{2}$	$\frac{2085}{2}$	−595	—	$\frac{5}{2}$	$\frac{40}{3}$	$-\frac{705}{4}$	1395	−1990	6	2	4227.2	678.9
"	3	—	—	—	—	11770	−51990	—	—	—	—	11770	−63760	7.1	6	3642.0	
12.38%/15′	1	—	$\frac{40}{3}$	0	$\frac{290}{3}$	200	0	—	$\frac{10}{3}$	$-\frac{40}{9}$	55	90	−90	5.5	0	4301.2	731.2
"	2	—	—	—	—	10350	−41005	—	—	—	—	10350	−51355	6.9	5.5	4473.0	

TABLE 2—*continued*

Sample	Function	Tensile strength, $T(E+1)$						Resilient energy						Limits of E		Resilient energy	
		Coefficients of:						Coefficients of:								Functional in.-lbs. per cu. in.	Total ft.-lbs. per cu. in.
		E^5	E^4	E^3	E^2	E	No.	E^5	E^4	E^3	E^2	E	$\text{Log}_e(E+1)$	Upper	Lower		
15.52%/15′	1	—	$\frac{40}{3}$	$\frac{40}{3}$	$\frac{110}{3}$	$\frac{1490}{3}$	0	—	$\frac{10}{3}$	0	$\frac{55}{3}$	460	−460	5	0	4017.4	626.6
"	2	—	—	—	160	6980	−24760	—	—	—	80	6820	−31580	6.2	5	3501.6	
18.15%/15′	1	—	$\frac{10}{3}$	$\frac{170}{3}$	$\frac{415}{6}$	$\frac{3185}{6}$	0	—	$\frac{5}{6}$	$\frac{160}{9}$	$\frac{95}{12}$	515	−515	4.5	0	3550.5	583.4
"	2	—	—	—	—	5440	−14090	—	—	—	—	5440	−19530	6	4.5	3450.2	
20.8%/15′	1	—	—	$\frac{280}{3}$	180	$\frac{1280}{3}$	0	—	—	$\frac{280}{9}$	$\frac{130}{3}$	340	−340	5.1	0	6373.2	531.1
23.2%/15′	1	—	—	60	350	340	0	—	—	20	145	50	−50	4.8	0	5704.7	475.4
28.7%/15′	1	—	—	—	590	505	0	—	—	—	295	−85	85	3.8	0	4070.2	339.2
1.98%/20′	1	—	—	$\frac{40}{3}$	40	$\frac{170}{3}$	0	—	—	$\frac{40}{9}$	$\frac{40}{3}$	30	−30	2	0	115.9	
"	2	$\frac{20}{3}$	$-\frac{260}{3}$	$\frac{1475}{3}$	$-\frac{3895}{3}$	$\frac{5780}{3}$	−1040	$\frac{4}{3}$	$-\frac{70}{3}$	195	$-\frac{2825}{3}$	3810	−4850	7	2	3959.7	407.4
"	3	—	—	—	—	19640	−11830	—	—	—	—	19640	137940	7.3	7	813.0	
5.70%/20′	1	—	—	$\frac{140}{3}$	10	$\frac{430}{3}$	0	—	—	$\frac{140}{9}$	$-\frac{55}{3}$	180	−180	2	0	213.4	
"	2	$\frac{32}{3}$	−140	$\frac{2300}{3}$	−1905	$\frac{8333}{3}$	−1480	$\frac{32}{15}$	$-\frac{113}{3}$	$\frac{2752}{9}$	$-\frac{8467}{6}$	5600	−7080	6.5	2	4314.0	602.8
"	3	—	—	—	—	17780	−95850	—	—	—	—	17780	113630	7.3	6.5	2706.0	
9.17%/20′	1	—	—	$\frac{100}{3}$	10	$\frac{680}{3}$	0	—	—	$\frac{100}{9}$	$-\frac{35}{3}$	250	−250	2	0	267.5	652.0
"	2	—	20	$-\frac{380}{3}$	735	$-\frac{4135}{3}$	1280	—	5	$-\frac{440}{9}$	$\frac{2645}{6}$	−2260	3540	7.0	2	7556.8	

TABLE 2—*continued*

TABLE 2—*continued*

Sample	Function	Tensile strength, $T(E+1)$						Resilient energy						Limits of E		Resilient energy	
		Coefficients of:						Coefficients of:								Functional in.-lbs. per cu. in.	Total ft.-lbs. per cu. in.
		E^5	E^4	E^3	E^2	E	No.	E^5	E^4	E^3	E^2	E	$\text{Log}_e(E+1)$	Upper	Lower		
12.38%/20′	1	—	—	40	40	210	0	—	—	$\frac{40}{3}$	0	210	−210	2	0	296.0	596.5
"	2	—	30	−170	$\frac{1325}{2}$	$-\frac{1425}{2}$	555	—	$\frac{15}{2}$	$-\frac{200}{3}$	$\frac{1725}{4}$	−1575	2130	6.5	2	6861.6	
15.52%/20′	1	—	$\frac{40}{3}$	$\frac{40}{3}$	$\frac{170}{3}$	$\frac{1100}{3}$	0	—	$\frac{10}{3}$	0	$\frac{170}{3}$	310	−310	5	0	3786.2	572.2
"	2	—	—	—	—	8820	−30520	—	—	—	—	8820	−39340	6.1	5	3078.8	
18.15%/20′	1	—	$\frac{40}{3}$	0	$\frac{410}{3}$	470	0	—	$\frac{10}{3}$	$-\frac{40}{9}$	75	320	−320	4	0	2533.9	543.4
"	2	—	—	—	—	5930	−15820	—	—	—	—	5930	−21750	5.7	4	3986.3	
20.8%/20′	1	—	—	$\frac{280}{3}$	180	$\frac{1220}{3}$	0	—	—	$\frac{280}{9}$	$\frac{260}{3}$	320	−320	5.0	0	6007.2	500.6
23.2%/20′	1	—	—	$\frac{160}{3}$	320	$\frac{1400}{3}$	0	—	—	$\frac{160}{9}$	$\frac{400}{3}$	200	−200	4.6	0	5127.2	427.3
28.7%/20′	1	—	—	—	630	525	0	—	—	—	315	−105	105	3.7	0	4086.4	340.5
0%/30′	1	—	—	$\frac{40}{3}$	20	$\frac{200}{3}$	0	—	—	$\frac{40}{9}$	$\frac{10}{3}$	60	−60	2	0	103.0	
"	2	$\frac{4}{3}$	$-\frac{20}{3}$	$\frac{35}{3}$	$\frac{335}{3}$	−168	180	$\frac{4}{15}$	−2	$\frac{59}{9}$	46	−260	440	7	2	3101.0	457.7
"	3	—	—	—	—	10080	−56080	—	—	—	—	10080	−66160	8.0	7	2283.3	
1.98%/30′	1	—	—	$\frac{80}{3}$	40	$\frac{160}{3}$	0	—	—	$\frac{80}{9}$	$\frac{20}{3}$	40	−40	2	0	133.9	
"	2	4	$-\frac{140}{3}$	$\frac{745}{3}$	$-\frac{1375}{3}$	$\frac{1688}{3}$	−180	$\frac{4}{5}$	$-\frac{38}{3}$	$\frac{897}{9}$	$-\frac{1136}{3}$	1320	−1500	7	2	4687.1	471.1
"	3	—	—	—	—	13600	−74600	—	—	—	—	13600	−88200	7.3	7	832.3	

TABLE 2—*continued*

Sample	Function	Tensile strength, $T(E+1)$						Resilient energy						Limits of E		Resilient energy	
		Coefficients of:						Coefficients of:								Functional in.-lbs. per cu. in.	Total ft.-lbs. per cu. in.
		E^5	E^4	E^3	E^2	E	No.	E^5	E^4	E^3	E^2	E	$\text{Log}_e(E+1)$	Upper	Lower		
5.70%/30′	1	—	—	$\frac{100}{3}$	0	$\frac{395}{3}$	0	—	—	$\frac{100}{9}$	$-\frac{50}{3}$	165	−165	3	0	416.3	495.6
"	2	—	20	−140	555	−745	580	—	5	$-\frac{160}{3}$	$\frac{715}{2}$	−1460	2040	7.3	3	5530.6	
9.17%/30′	1	—	—	$\frac{40}{3}$	80	$\frac{470}{3}$	0	—	—	$\frac{40}{9}$	$\frac{100}{3}$	90	−90	2	0	250.0	576.2
"	2	—	20	−100	355	−215	230	—	5	−40	$\frac{475}{2}$	−690	920	7.0	2	6664.9	
12.38%/30′	1	—	—	$\frac{80}{3}$	60	$\frac{490}{3}$	0	—	—	$\frac{80}{9}$	$\frac{50}{3}$	130	−130	2	0	255.0	545.5
"	2	—	$\frac{100}{3}$	$-\frac{620}{3}$	$\frac{2255}{3}$	$-\frac{2605}{3}$	630	—	$\frac{25}{3}$	−80	$\frac{2975}{6}$	−1860	2490	6.5	2	6291.0	
15.52%/30′	1	—	10	$\frac{70}{3}$	$\frac{55}{2}$	$\frac{2155}{6}$	0	—	$\frac{5}{2}$	$\frac{40}{9}$	$\frac{85}{12}$	345	−345	5	0	3402.0	505.1
"	2	—	—	—	80	6520	−22750	—	—	—	40	6440	29190	6.1	5	2659.0	
23.2%/30′	1	—	—	$\frac{160}{3}$	360	$\frac{1220}{3}$	0	—	—	$\frac{160}{9}$	$\frac{460}{3}$	100	−100	4.6	0	5262.6	438.6
28.7%/30′	1	—	—	—	680	520	0	—	—	—	340	−160	160	3.6	0	4074.6	339.6

$$\text{Resilient energy of 5.70 per cent/5}' = \frac{1}{12}(101.8 + 4244.1 + 608)$$

$$= \frac{1}{12}(4953.9)$$

$$= 412.8 \text{ foot-lbs. per cubic inch.}$$

The coefficients of E in Table 2 refer to the inch-lb./cu. in. system of units; the total resilient energy is obtained in these units and divided by 12 to give the resilient energy in the last column as foot-lbs. per cubic inch.

Partial resilient energies.—The total resilient energy of the samples, as given in the last column of Table 2, was plotted on graphs of Figures 1 and 2. By the same graphical method and from separate, large graphs, the following total resilient energies and partial resilient energies of base mix and of filler were obtained for various percentages of filler as shown in Table 3.

TABLE 3

TOTAL AND PARTIAL RESILIENT ENERGIES: PERCENTAGES OF FILLER

Cure (min.)	2.5 per cent			5 per cent			10 per cent		
	R	R_B	R	R	R_B	R_F	R	R_B	R_F
5	...	...	...	...	...	...	630	295	3650
10	488	355	5700	592	440	3500	700	560	1920
15	488	190	12100	617	450	3800	720	635	1500
20	508	337	7200	595	425	3800	645	785	−610
30	482	432	2450	525	448	2000	568	690	−530

Cure (min.)	15 per cent			20 per cent			25 per cent		
	R	R_B	R_F	R	R_B	R_F	R	R_B	R_F
5	706	690	790	506	1160	−2100	369	950	−1350
10	677	1080	−1600	532	1000	−1350	424	910	−1040
15	660	1170	−2250	540	900	− 890	438	900	− 960
20	558	785	− 730	483	755	− 600	420	720	− 480
30	510	675	− 420	457	660	− 360	408	650	− 315

The calculations of resilient energy were confirmed by the use of the trapezoidal rule, by which a direct integration is obtained from the numerical results for the tensile strength, T; the rule is:

$$R = h(0 + T_1 + T_2 + T_3 + \cdots + \tfrac{1}{2}T_n)$$

where $h = 1$ = the interval at which values of T are taken and T_1, T_2, etc., are values of T at an elongation of each successive inch. When a sample breaks at a fractional elongation, *e.g.*, 7.2 inches per inch, the expression is divided into two parts, $E = 0 - 7.0$ and $E = 7.0 - 7.2$; the resilient energy, R, is obtained for each part, and these values of R are added to give the total resilient energy.

According to the interpretation of the partial resilient energies of base mix and of filler given in this communication, these quantities are solely a mathematical idea and are devoid of any physical meaning; they fulfil the requirements of Equation (4) in which, by substitution of their numerical values, the total resilient energy of the mix or sample may be obtained. The large variation in values for the partial resilient energy of the reinforcing agent used in this instance is caused by the substantial reinforcement which is given by small percentages of this ingredient. A possible use for this quantity, R_F, may be found in predicting the total resilient energy of a compound containing several

reinforcing agents for which the partial resilient energies are known. The curves in Figure 1 giving total resilient energies at different periods of cure are similar to one another.

From the scientific, as distinct from the technological, point of view, the division of the tensile curve into three portions, as predicted by Mark, is shown by compounds containing a small amount of the reinforcing agent. However, this cannot be regarded as a proof that the processes mentioned by Mark actually take place. For more heavily loaded compounds, the three portions may overlap so far that they become two or even one, as if larger proportions of the ingredient had the effect of suppressing some stages or causing the stages to operate concurrently.

SUMMARY

1. The tensile strength of vulcanized rubber may be expressed in terms of its elongation by means of the calculus of finite differences.

2. This expression for tensile strength, based on the theoretical cross-sectional area, gives an expression for the tensile strength based on the original cross-sectional area when the former quantity is divided by the factor $(E + 1)$, E being the elongation.

3. The expression for tensile strength based on the original cross-sectional area is integrated with respect to the elongation to give the resilient energy.

4. The trapezoidal rule has proved itself to be superior to the calculus of finite differences as a practical method of obtaining the resilient energy.

5. The total resilient energies are plotted on graphs against the percentage by volume of reinforcing agent or filler. Tangents drawn at any desired point corresponding to a certain percentage of filler give values for the partial resilient energies of base mix and of filler by the method of tangent intercepts.

6. The expressions for tensile strength are composed of one, two or three functions; the number of functions is, in general, inversely proportional to the percentage of the filler in the vulcanizate.

7. The expressions for tensile strength and for resilient energies have no significance regarding the structure of vulcanized rubber; they have been evolved from the point of view of usefulness for evaluating compounds.

8. The values of the partial resilient energies of base mix and of filler obtained by the method of tangent intercepts have no physical meaning; they are a means of calculating the total resilient energy of a sample of vulcanized rubber.

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BRITTLE TEMPERATURE OF RUBBER UNDER VARIABLE STRESS *

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The projected use of synthetic elastomers on a large scale for outdoor service presents a pressing need for information dealing with their properties at subzero temperatures. Under extreme cold weather conditions, insulation, cable jackets, tires, tubes, and many other items must be capable of being repeatedly flexed without failure at temperatures of −50° C or lower.

In a previous paper[1] a method was presented for determining the critical temperature of fracture, where the sample is bent rapidly through an angle of approximately 90°. Although this test provides an excellent technique for the comparison of various rubber compositions, it was realized that the procedure should be revised to include the effect of varying the magnitude of stress as well as the rate of bending to simulate more closely certain types of service. The present paper does this, and also reviews some of the work already carried out in the field of low-temperature rubber testing.

Early investigation[2] showed that crude rubber increased in tensile strength at low temperatures. Le Blanc and Kröger[3] described this phenomenon as cold vulcanization. The observation that rubber which had been elongated and cooled in liquid air could be disrupted into fibrous fragments was reported by Hock[4]. Mark and Valko[5] associated this phenomenon with brittleness, and conducted experiments which showed that, under given test conditions, the "critical point" of raw rubber was −67° C.

Ruhemann and Simon[6] observed that a sharp rise in the specific heat of smoked sheet rubber occurred in the range −65° to −75° C.

Bekkedahl[7] found that at −70° C a sharp change of slope occurs in the temperature-volume curve with both supercooled amorphous and crystalline raw rubbers. This observation is important because it demonstrates that the state of brittleness develops at the same point independently of the existence of either physical state. Differences in the brittle points of crystalline and amorphous smoked sheet rubber, as determined by the fracture method described in the previous work[1], were found to be slight.

Aside from the fracture method[8] other procedures used in investigations of rubber at low temperatures may be grouped according to the method of test into three general types involving deflection[9], penetration[10] and elastic deformation[11]. The method of Koch[12] may be considered a representative test for measuring the resistance to deflection of an elastic material at low temperatures. Penetration measurements by a dead-weight indentation method as reported by Nagai[10] represent this type of low temperature test. The work of Sagajllo, Bobinska and Saganowski[13] demonstrated the combined effects of elastic deformation and temperature lowering on rubber. This testing procedure is similar to the T-50 method[14] commonly used for determining the state of vulcanization in certain flat-curing carbon black-reinforced rubber compounds; the interpretation of the data is the important difference.

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Although deflection, penetration, and elastic deformation tests detect appreciable changes in certain properties of rubber at low temperatures, it would be difficult to predict the performance of a given material tested by these methods with reference to its being subjected to a sudden bending stress. The deflection method used by Koch[12] defines the point of maximum stiffness in rubber, and gives indications of increased resistance to deformation at temperatures above the brittle point, but would not permit the prediction of how a given material would respond to severe or rapid mechanical deformation in service. The data published by Nagai[10] on decreasing penetration values observed with lowering of the temperature are of little value aside from furnishing a rough indication of increased hardness under these conditions. It will be shown later that hardness tests do not correlate with brittleness tests on bending.

APPARATUS AND METHOD

In the improved apparatus shown in Figure 1, the quadrant, *A*, upon which the fixtures, *B*, for varying the bending stress are mounted, is rotated by a worm drive, *C*, which utilizes interchangeable gears to vary the rate of defor-

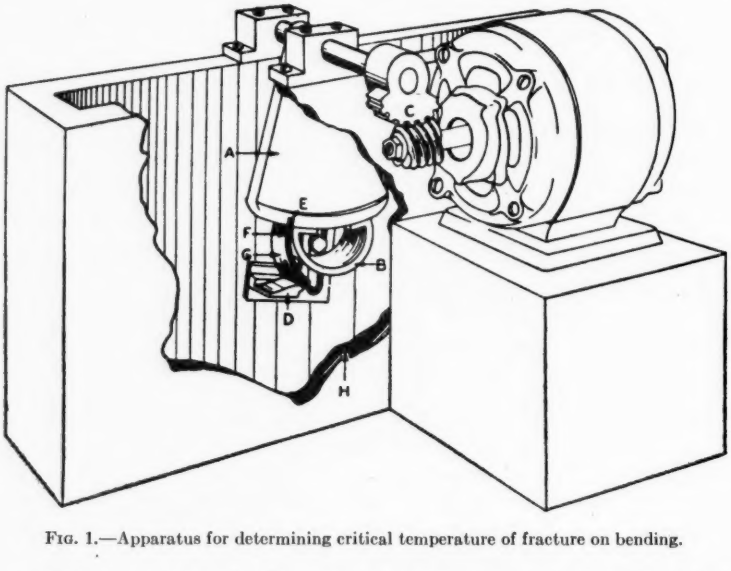

FIG. 1.—Apparatus for determining critical temperature of fracture on bending.

mation. This mechanism is driven by a 1/12-horsepower squirrel-cage motor, operating at 1140 r.p.m. and using a four-thread twelve-pitch worm wheel of thirty teeth with 2.5-inch (6.35-cm.) pitch diameter and a sixty-tooth 5-inch (12.7-cm.) pitch diameter wheel with a corresponding worm gear; this arrangement gives quadrant speeds of 150 and 75 r.p.m. The fast speed was selected on the basis of duplication of results obtained for a large variety of rubber and synthetic elastomer compositions in tests using the manually operated apparatus previously described[1]. The right-angle bend is obtained by setting the rigid breaking arm, *D*, 0.25 inch (6.3 mm.) beyond the arc described by a block 0.25 inch square; the block is mounted on the periphery of the quadrant and flush with the back of the slot, *E*, in which the test-specimen, *F*, is inserted.

When testing by the application of a bending stress controlled in intensity by a selected arbor, a strip of 0.01-inch (0.254-mm.) spring steel, *G*, is inserted in the slot before the test-specimen; the clearance of the breaking arm is adjusted so that in the test cycle the sample is bent rapidly to conform with the profile of the arbor. The immersion tank is insulated, *H*, by a double wrapping of aluminum foil, a 0.5-inch (1.27-cm.) layer of fiber glass, and an asbestos board enclosure. At the brittle fracture point, determined by rotation at the fast speed with an arbor of 1-inch (2.54-cm.) radius, three or four breaks usually occur in a specimen 1.5 inches (3.81 cm.) in length, and a temperature is found where a given material will be intact after a bending cycle, but will fail when this temperature is lowered 1° C. When this point is determined, five specimens are tested successively at a temperature 1° C above the point of failure; if all are intact after being put through the test cycle, the brittle fracture point is stated as the temperature between the observed points of survival and failure. A calibrated Weston dial thermometer was used for temperature measurements in this work.

Experience in manipulating the acetone-solid carbon dioxide conditioning bath has shown that certain precautions are necessary to assure accurate temperature control. The procedure consists of placing 3.5 pounds (1.59 kg.) of crushed solid carbon dioxide in the insulated tank which is $14 \times 2 \times 8$ inches ($35.56 \times 5.08 \times 20.32$ cm.) and adding acetone in small quantities until a saturated solution is obtained, as indicated by a temperature of $-78°$ C. Circulation is then induced by a motor stirrer, and the total acetone added is increased to 2 liters. Approximately 30 minutes are required to reach a condition of equilibrium where an immediate lowering of the temperature is noted on the addition of a small quantity of the pulverized refrigerant. The quantities of a refrigerant and liquid mentioned produce an equilibrium temperature of approximately $-70°$ C. In determining the brittle fracture point, it is standard practice to establish the approximate temperature of failure by preliminary tests at 10° C intervals and then continue testing at 1° C ascending intervals until the temperature of survival is noted. The heat transfer in the system resulting from inserting a test-specimen and reimmersing the quadrant produces a rise of less than 1° C, and the temperature rise between $-60°$ and $-50°$ C averages about 0.25° C per minute. Exactly 5 minutes are allowed for the conditioning of each test-specimen except in the case of highly plasticized materials, such as Koroseal and Vinylite, which are tested after a 2-minute immersion to minimize the possible effects of solvent action on their structure. The use of both acetone and ethyl alcohol as cooling media have been found to produce results which check closely with those from similar tests conducted in an air atmosphere after longer conditioning periods.

BRITTLE TEMPERATURE OF RUBBER COMPOSITIONS

Table I contains brittle fracture point data for pure gum and high-quality mechanical rubber compositions tested under controlled conditions of variable bending stress and rate of deformatoin. The results as stated were found by numerous check tests on the same materials to be reproducible within $\pm 0.5°$ C. It was shown, however, in our previous work that raw rubber from different sources varies in brittle point over a range of about 4° C, which results in a wider limit of reproducibility from batch to batch.

With the decreased magnitude of the bending stress and rate of deformation, the pure-gum vulcanizate does not fail at $-78°$ C, but the brittle fracture

point of the carbon-black-reinforced rubber is lowered only 6.5° C by the less severe conditions of test, and a further decrease in rate of deformation by using a quadrant speed of 37.5 r.p.m. failed to lower further the temperature of fracture for the latter material.

TABLE I

EFFECTS OF VARIABLE BENDING STRESS AND RATE OF DEFORMATION ON BRITTLE FRACTURE POINTS OF RUBBER VULCANIZATES

Compound No.	1	2
Smoked sheet	100.00	100.00
Mercaptobenzothiazole	0.50	0.75
Zinc dimethyldithiocarbamate	...	0.10
Sulfur	3.50	3.00
Stearic acid	0.50	2.00
Zinc oxide	6.00	10.00
Channel black	...	30.00
Semireinforcing black	...	30.00
Phenyl-α-naphthylamine	...	2.00
Sunlight aging inhibitor	...	2.00
Cure in min. (° C)	80(126)	20(141.5)

Rate of deformation (quadrant speed) (r.p.m.)	Radius of bending stress (cm.)	Brittle fracture point (° C)	
		Pure gum	Carbon black stock
150	Right angle	−56.5	−58.5
	2.54	−61.5	−60.5
	3.81	[a]	−63.5
75	Right angle	−58.5	−60.5
	2.54	−61.5	−62.5
	3.81	[a]	−65.0

[a] No failures observed at −78° C.

Brittle fracture point data under variable stress for a series of reclaimed rubber compositions (Table II) showing the effects of adding semireinforcing black, clay and whiting, mineral oil, blown asphalt, and smoked sheet. The brittle point of the uncompounded reclaimed rubber was −49° C. These data show that the temperature of fracture varies with both the speed and magnitude of the bending stress.

As previously found[1], the nature of the rubber used is more important than minor changes in the composition. Undoubtedly lower speeds or less severe bending stresses than those employed in these tests would result in still lower temperatures at which these compositions would fracture.

BRITTLE TEMPERATURE OF SYNTHETIC ELASTOMERS

In view of the increasing amounts of synthetic elastomers now becoming available to the rubber industry and the immediate possibility of their extensive use, the need for information pertaining to their low-temperature properties becomes urgent. In contrast to rubber, considerable improvement may be effected in some of these materials by the use of certain compounding ingredients. Wide variations in brittle points were observed during the previous work[1] in different types of the same general class of material, as well as in the same material from different sources.

Synthetic thermoplastic elastomers.—Considerable information is available on the low-temperature properties of polyvinyl chloride which, although a hard

plastic at room temperature, can be converted into a flexible and elastic material by the incorporation of chemical plasticizers in sufficiently large quantities. Russell[15] reported that the μ form of polyvinyl chloride is brittle at 81° C, but that a mixture consisting of 60 parts of this material and 40 parts of dibutyl phthalate by weight (Koroseal) exhibited a brittle point of −46° C. His method for brittle point determination consisted of conditioning bars of the materials for 5 minutes in an alcohol bath at the temperatures stated, removing them, and immediately bending them double.

TABLE II

BRITTLE FRACTURE POINTS OF ALL-RECLAIM AND LOW-RUBBER-CONTENT COMPOSITIONS[a]

Compound No.		3	4	5	6	7	8
Whole tire reclaim		67.50	67.50	67.50	67.50	62.50	57.50
Semireinforcing black		21.65	...	...	21.65	21.65	21.65
Hard clay		...	31.00	...	...	...	...
Ground limestone		...	...	32.40	...	...	...
Light-process oil		7.00	7.00	7.00	...	7.00	7.00
Mineral rubber (m. p. 310° F or 154° C)		...	...	...	7.00	...	...
Sulfur		1.00	1.00	1.00	1.00	1.00	1.00
Tetramethylthiuram monosulfide		0.15	0.15	0.15	0.15	0.15	0.15
Di-*o*-tolylguanidine		0.10	0.10	0.10	0.10	0.10	0.10
Sunlight aging inhibitor		2.00	2.00	2.00	2.00	2.00	2.00
Antioxidant		0.30	0.30	0.30	0.30	0.30	0.30
Smoked sheet		...	...	...	...	5.00	10.00
Rate of deformation (quadrant speed) (r.p.m.)	Radius of bending stress (cm.)	Brittle fracture point, ° C					
150	Right angle	−47.5	−46.5	−47.0	−43.5	−47.5	−50.0
	2.54	−50.5	−51.5	−51.5	−46.0	−51.5	−51.5
	3.81	−52.5	−53.5	−53.5	−49.5	−53.5	−55.5
75	Right angle	−50	−49.5	−49.5	−44.5	−51.0	−51.5
	2.54	−51.5	−55.5	−53.5	−46.0	−52.5	−53.5
	3.81	−54.5	−57.5	−56.5	−50.0	−54.5	−56.5

[a] Cured 20 minutes at 141.5° C.

Fuoss[16] observed that plasticized polyvinyl chloride behaves similarly to rubber in that, at a certain definite temperature, a sudden change in mechanical and electrical properties is noted. He refers to this point at which brittleness occurs as an internal melting point. Since the unplasticized material is in a general class of hard plastics, including cellulose acetate and polystyrene which are also extensively used in their unplasticized form and as such are evaluated by their resistance to plastic flow, this terminology is correct. However, in the case of the plasticized materials which are useful in their flexible and elastic condition, the term "brittle point" is a more significant designation. Davies, Miller, and Busse[17], also studying the electrical properties of this material, stated that three variables—temperature, frequency of current, and ratio of plasticizer to polyvinyl chloride—can be made to produce roughly equivalent results. The chemical significance of plasticizer action on these materials is beyond the scope of this work; however, reference may be made to the work of Houwink[18] who suggests that the brittleness of a substance will depend upon the distance over which the interacting molecular forces work. Considerable

insight on the mechanics of plasticizer action with particular reference to cellulose acetate is given in a recent article by Gloor and Gilbert[19].

Table III lists brittle fracture data for plasticized polyvinyl chloride and polyvinyl chloride-acetate copolymers which may be considered average materials of their types. The samples tested were strips 1.75 × 0.5 × 0.075 inch (4.45 × 1.27 × 0.19 cm.) cut with scissors from sheets molded from the calendered materials under a pressure of 500 pounds per square inch (89.25 kg. per sq. cm.) for 5 minutes at 141.5° C and cooled for 5 minutes under pressure.

TABLE III

BRITTLE FRACTURE POINTS OF PLASTICIZED POLYVINYL CHLORIDE AND POLYVINYL CHLORIDE-ACETATE COPOLYMER

Rate of deformation (quadrant speed) (r.p.m.)	Radius of bending stress (cm.)	Brittle fracture point (° C)	
		Polyvinyl chloride polymer 9	Polyvinyl chloride-acetate copolymer 10
150	Right angle	−25.5	−50.0
	2.54	−32.5	−70.5
	3.81	−46.5	[a]
75	Right angle	−30.0	−56.0
	2.54	−38.5	−72.0
	3.81	−51.5	[a]

[a] No failures observed at −78° C.

The immersion time in the acetone-solid carbon dioxide bath was exactly 2 minutes for each test, and the brittle fracture points stated were verified by the observation of five consecutive cases of survival at temperatures 0.5° C above the stated points. Some difficulty was encountered in testing these materials. In the various test cycles occasional cases of nonfailure were observed as much as 10° C lower than the brittle fracture points stated; thus there is the possibility of a heterogeneous condition in plasticized mixtures of the types investigated.

Vulcanizable synthetic elastomers.—Synthetic elastic polymers which more closely resemble rubber include butadiene polymers, acrylonitrile and styrene copolymers of butadiene, polychloroprene and its diolefin copolymers, polyisobutylene and its diolefin copolymers, and various types of organic polysulfides. These materials, mixed in various proportions with vulcanizing agents and typical rubber compounding ingredients and vulcanized by heating, exhibit widely varying low-temperature properties[1], owing to their different chemical structures. Koch[12] applied his deflection test to an undisclosed butadiene-styrene copolymer composition and observed a freezing point of −66° C, which is in agreement with the brittle point range of −66° to −70° C for this material observed in the previous work[1]. Bekkedahl and Scott[20] recently reported a second-order transition point of −23° C for Hycar-OR (modified butadiene-nitrile copolymer), using the technique previously described in their work on rubber. These authors also stated that no first-order transition was observed in the material studied. The brittle point of this material was found in our earlier work to be about −25° C. Garvey, Juve, and Sauser[21] reported low-temperature observations for a number of Hycar-OR compositions.

Table IV shows the brittle fracture points under variable stress of three butadiene-styrene copolymer compositions. These results are similar to those in Table I in respect to the effect of varying the nature of the stress. It was

previously shown[1] that a good Buna-S tire tread stock (without the blown asphalt) had a brittle fracture point of −66° to −70° C under a right-angle bend at high speed. These results show that the brittle temperature of synthetic rubber is more sensitive to compounding than natural rubber. For this

TABLE IV

BRITTLE FRACTURE POINTS OF BUNA S COMPOSITIONS[a]

Compound No.		11	12	13
Buna S		100.00	50.00	50.00
Smoked sheet		...	50.00	25.00
Whole tire reclaim		...	...	50.00
Carbon black (special)		50.00	50.00	50.00
Blown asphalt		25.00	25.00	25.00
Sulfur		2.00	2.00	2.00
Stearic acid		2.00	2.00	2.00
Zinc oxide		15.00	15.00	15.00
Accelerator A		1.00	1.00	1.00
Accelerator B		1.50	1.50	1.50
Rate of deformation (quadrant speed) (r.p.m.)	Radius of bending stress (cm.)	Brittle fracture point (° C)		
150	Right angle	−51.5	−51.5	−49.5
	2.54	−54.5	−52.5	−51.5
	3.81	−59.5	−58.5	−53.5
75	Right angle	−54.5	−55.5	−51.5
	2.54	−58.5	−56.5	−53.5
	3.81	−63.5	−60.5	−57.0

[a] Cured 20 minutes at 141.5° C.

reason greater care must be taken in compounding Buna-S for low-temperature service.

Yerzley and Fraser[22] recently investigated the effects of low temperatures on the Shore A hardness, elastic deformation, and mechanical deflection (torsion) of neoprene compositions; they proposed the term "freeze factor" to express the ratio of the observed change in hardness produced by low temperatures to the maximum possible increase in hardness for a given material.

TABLE V

COMPARISON OF LOW-TEMPERATURE PROPERTIES OF NEOPRENE FR COMPOSITIONS[a] AS DETERMINED BY SHORE A HARDNESS AND BRITTLE FRACTURE TESTS

Compound No.	Softener (30 parts by wt.)	F-50 temp. (° C)	Brittle fracture point[b] (° C)	Hardness at brittle fracture point
14	Diisobutyl adipate	−54	−58.5	80
15	Dibutyl phthalate	−46	−61.5	92
16	Coal-tar softener	−43	−50.5	93
17	Dibutyl sebacate	−40	−66.5	92
18	Light-process oil	−38	−53.0	95

[a] Base formula: Neoprene FR 100.0, stearic acid 1.0, Neozone A 2.0, soft black 100.0, sulfur 1.0, litharge 10.0.

[b] Rate of deformation, 150 r.p.m.; right-angle bend.

A new interpretation of this effect, designated as "F-50"[23], was recently proposed to define the temperature where half the maximum possible increase in Shore A hardness is observed.

A comparison of data obtained by Shore A hardness measurements and brittle fracture point tests for the same series of Neoprene FR compositions is shown in Table V along with the Shore A hardness values for the various compositions at their respective brittle fracture points. The fracture test indicates that compound 17, containing 30 parts of dibutyl sebacate, would be serviceable at a temperature 5° C lower than the best of the series as indicated by the hardness observations. Composition 17, subjected to bending tests at a quadrant speed of 37.5 r.p.m. over a 3.8-cm. radius arbor, showed no failure at −76° C; compound 14 exhibited a brittle fracture point under these conditions at −67° C.

The addition of dibutyl sebacate and diisobutyl adipate resulted in an appreciable lowering of the brittle fracture points of a typical Neoprene GN composition (Table VI); the order of improvement was the same as in the

TABLE VI

BRITTLE FRACTURE POINTS OF NEOPRENE GN COMPOSITIONS

Compound No.		19	20	21
Neoprene GN		100.0	100.0	100.0
Magnesium oxide		7.0	7.0	7.0
Zinc oxide		2.0	2.0	2.0
Antioxidant		1.0	1.0	1.0
Semireinforcing black		35.0	35.0	35.0
Petroleum softeners		2.0	2.0	2.0
Stearic acid		0.25	0.25	0.25
Accelerator		0.25	0.25	0.25
Diisobutyl adipate		...	15.0	...
Dibutyl sebacate		...	...	15.0
Rate of deformation (quadrant speed) (r.p.m.)	Radius of bending stress (cm.)	Brittle fracture point (° C)		
150	Right angle	−41.5	−51.5	−55.5
	2.54	−45.5	−56	−58.5
	3.81	−46.5	−57	−60
75	Right angle	−43	−54	−57
	2.54	−46.5	−56	−59
	3.81	−50.5	−58	−62

series of tests with Neoprene FR compounds. Cooling curves made for the two plasticizers showed that both are in a solid state at temperatures above the fracture points of the compounds in which they were used, and that freezing occurs well within the conditioning time allowed according to the testing procedure. Swelling tests on vulcanized base compound 19 in diisobutyl adipate and dibutyl sebacate showed appreciable increases in weight after 12-hour immersion at 60° C. The Neoprene immersed in dibutyl sebacate increased 80 per cent by weight as compared to a 70 per cent increase for the sample immersed in diisobutyl adipate. On the basis of these observations and the brittle fracture test results, it appears that increased solvent action may offer a better guide to the selection of materials for lowering the brittle fracture point than the freezing point observations on the plasticizers.

CONCLUSIONS

1. The temperature at which natural and synthetic elastomers fracture on bending depends on the rate of application and the magnitude of the stress applied. The slower the rate of bending and the less the angle of bend, the lower will be the temperature of fracture.

2. A study of the stresses under varying types of service at subzero temperatures must be made in order to select intelligently the laboratory test conditions which will best simulate performance in the field.

3. In the case of synthetic elastomers having high fracture temperatures, the addition of certain types of plasticizers serve to correct this difficulty.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of W. H. Lockwood who performed a large part of the testing in connection with this paper.

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PREVENTING THE BACTERIAL OXIDATION OF RUBBER*

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The recent article by ZoBell and Grant[1] notes the attack of rubber by bacteria under conditions of high moisture. It is suggested that "the life of rubber products which come in contact with moisture may be prolonged if ways can be found to retard or prevent the activity of rubber oxidizing micro-organisms".

In the compounding of rubber commercially, native rubber is mixed with a number of chemicals, each of which serves a specific purpose in the properties of the finished product. Among these are accelerators[2] which lower the temperature and shorten the time of vulcanization and lengthen the life of rubber.

Two well-known accelerators are mercaptobenzothiazole and tetramethylthiuram disulfide. These compounds have been tested for their ability to inhibit germination of fungi, and gross observations have been made on their ability to inhibit bacterial growth. Mercaptobenzothiazole is a moderately good fungicide, and tetramethylthiuram disulfide is excellent. The latter compound is now being marketed as a seed protectant and for the prevention of turf diseases. Both of these materials have been tested, under field conditions prevailing in Connecticut, by the authors for their efficacy in controlling plant diseases. Mercaptobenzothiazole, although inferior to tetramethylthiuram disulfide, has given partial plant disease control.

These materials, when employed in the compounding of rubber, are intimately mixed with zinc oxide, which is itself a useful fungicide and seed protectant. From a knowledge of the formulas of these accelerators, it occurred to the authors that zinc oxide might react with mercaptobenzothiazole and with tetramethylthiuram disulfide, and that the reaction products might differ in their antimicrobial potency.

Spore germination tests were set up, using the method of Horsfall, Heuberger, Sharvelle and Hamilton[3]. Glass slides were sprayed with aqueous suspensions of mercaptobenzothiazole and tetramethylthiuram disulfide, with and without zinc oxide, and with suspensions of zinc oxide alone. Each type of suspension was sprayed in a dosage series. The glass slides were allowed to dry, after which drops of a suspension of spores of the fungus, *Macrosporium sarcinaeforme*, were placed on the dried residues of sprayed material. The slides were incubated for 18 to 20 hours, and then counts were made of the percentage inhibition of spore germination.

These tests indicate that, in compounding with zinc oxide, mercaptobenzothiazole becomes inactivated as a fungicide, whereas tetramethylthiuram disul-

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TABLE 1

EFFECT OF ADDING ZINC OXIDE TO MERCAPTOBENZOTHIAZOLE AND THEIR ABILITY TO INHIBIT THE GERMINATION OF FUNGOUS SPORES

Dosage of toxicant (γ per sq. cm.)		Percentage inhibition
Mercaptobenzothiazole		
864		100
432		96
216		4
108		1
Mercaptobenzothiazole + zinc oxide		
520	345	4
260	173	2
130	86	0
65	43	0
Zinc oxide		
864		100
432		100
216		98
108		94

TABLE 2

EFFECT OF ADDING ZINC OXIDE TO TETRAMETHYLTHIURAM DISULFIDE ON THEIR ABILITY TO INHIBIT THE GERMINATION OF FUNGOUS SPORES

Dosage of toxicant (γ per sq. cm.)		Percentage inhibition
Tetramethylthiuram disulfide*		
34.3		53
24.4		54
17.1		75
12.3		74
8.5		23
6.1		10
Tetramethylthiuram disulfide + zinc oxide		
8.6	69	99
6.1	49	50
4.3	34	24
3.1	25	15
2.2	17	6
Zinc oxide		
137		100
98		99
68		67
49		32

* The dosage-inhibition relation shown for tetramethylthiuram disulfide is characteristic[4].

fide does not. Since the presence of zinc oxide is absolutely essential to the successful compounding of rubber, it is evident that, when mercaptobenzothiazole is used as an accelerator in rubber, it is rendered wholly innocuous as an inhibitor of microörganisms, and that the resulting rubber will be susceptible to attack by microörganisms under the conditions noted by ZoBell and Grant[1].

On the other hand, it is evident that tetramethylthiuram disulfide retains a large part of its activity against microörganisms in the presence of zinc oxide.

That mercaptobenzothiazole, tetramethylthiuram disulfide and zinc oxide as such remain in vulcanized rubber is implied by the fact that their presence

in rubber can be estimated quantitatively[5]. We may, therefore, conclude that accelerators incorporated into rubber in vulcanization at least partly remain in the manufactured product. Any antimicrobial properties possessed by an accelerator would be a decided factor in preventing bacterial oxidation of rubber.

In view of these results, it is clear that, when rubber is to be used under conditions where it is likely to be in contact with water over long periods or even intermittently (as in the tropics), tetramethylthiuram disulfide should be used as an accelerator in preference to mercaptobenzothiazole, provided that other desirable properties of the resulting rubber are not sacrificed by this procedure.

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X-RAY STUDY OF REACTIONS INVOLVING ACCELERATORS

ORIENTATION OF CRYSTALLINE PHASES ON STRETCHING OF RUBBER STOCKS *

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About a year ago, in the course of a systematic survey of the x-ray diffraction patterns of a number of routine rubber samples with different accelerators present, certain similarities were noted in the diffraction effects from the accelerators in these stocks. Close examination of these effects showed that they were identical. The stocks contained the accelerators tetramethylthiuram disulfide, tetramethylthiuram monosulfide and zinc dimethyldithiocarbamate, which are chemically similar (Table I); the first is the disulfide, the second, the monosulfide, and the third, the zinc salt. Thus, the diffraction patterns indicate that, on curing, the disulfide and the monosulfide in the presence of sulfur react with zinc oxide to form the zinc salt. This is not a new concept. The zinc salts have been extracted with solvents from stocks similar to the above, and it has been supposed that such reactions occur. However, the extraction method leaves some doubt as to whether the salt was originally present in the rubber matrix or whether it was formed in the solvent on extraction.

Every crystalline material has its own characteristic x-ray diffraction pattern, which is different from that of every other crystalline material, just as the fingerprints of each person are different from those of every other person. Thus, with x-ray "fingerprint" patterns it is possible to identify positively the presence of these salts in the rubber matrix and show that they must have been formed in the rubber mix on curing. Further, it was noted that this crystalline salt is strongly oriented in the rubber matrix on stretching. It seemed advisable, then, to investigate other similar reactions by the x-ray method and to investigate the significance of the strong orientation of these reaction products in the rubber matrix.

EXPERIMENTAL PROCEDURE

The rubber stocks listed in Table I were prepared (in the Vanderbilt laboratory) and tested by the x-ray method (at the University of Illinois). Series A consists of stocks made up according to standard compounding practice. Series B was prepared with larger quantities of accelerator than are usually employed so that the reaction products would be larger in amount and thus more easily detected in the rubber matrix by the x-ray method. Series C is

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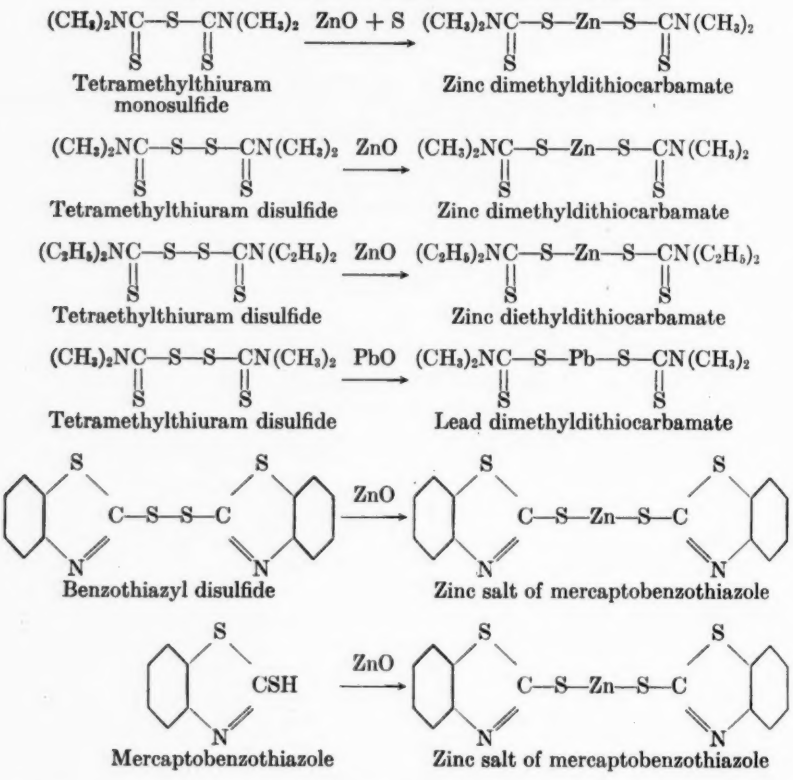
TABLE I

REACTIONS BETWEEN ACCELERATOR AND ACTIVATOR



the same as series B except that it contains no stearic acid. It was prepared to observe the effect of stearic acid on the chemical reactions between accelerator and activator.

The x-ray diffraction apparatus consisted of a Philips Metalix copper-target tube mounted in a Hayes multiple diffraction unit. The tube was operated at 28 kilovolts potential and 20 milliamperes. The radiation was filtered through one-mil nickel foil to remove the beta radiation. Agfa non-screen x-ray film was used, and developed in Eastman developer.

The rubber samples in most cases were cut from rubber slabs with scissors along the grain of the rubber to give a small sliver. This sliver was simply stretched over the pinhole of the collimating system, and a flat cassette exposure of 2 hours made at a sample film distance of 5 cm. In some cases dumbbell test-specimens were used, and the elongation was noted in the usual manner.

The RCA electron microscope at the University of Illinois was employed to determine the particle shape of some of the materials which showed themselves by the x-ray method to be strongly oriented in the rubber matrix on stretching. The sample screens of the electron microscope were prepared in the usual manner, with a film formed by dropping a dilute solution of collodion

in amyl acetate on water and then stripping the film from the water surface. The materials to be studied—for example, calcium carbonate, zinc oxide, lead dimethyldithiocarbamate—were dispersed in butanol, and the butanol dispersion was allowed to dry on the collodion film before the sample holder was placed in the electron microscope.

CHEMICAL REACTIONS

Table I gives the chemical reactions which occur in the rubber matrix at the curing temperature. The evidence for these reactions is presented in the form of x-ray diffraction patterns of the various stocks involved. Figure 1 shows a pattern of pure crepe rubber (free from all fillers and compounding agents); it is stretched nearly to break and taken with a monochromatized

TABLE II

RUBBER STOCKS[a] CURED 30 MINUTES AT 274° F

SERIES A

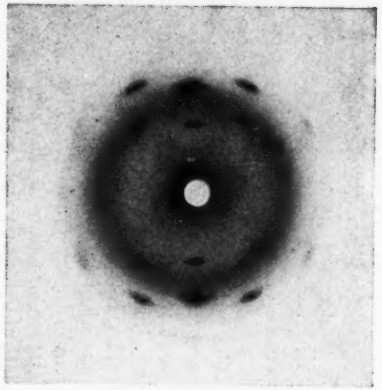
Material	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}
Smoked sheet	100	100	100	100	100	100	100	100	100	100
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	1
Zinc oxide	3	3	3	3	3	...	...	...	3	3
Sulfur	2	2	2	2	2	2	2	2	3	3
Zinc dimethyldithiocarbamate	0.5	...	...	...	...	...	...	...	...	...
Zinc diethyldithiocarbamate	...	0.5	...	...	...	...	...	...	...	...
Tetramethylthiuram disulfide	...	...	0.5	...	...	0.5	0.5	0.5	...	...
Tetraethylthiuram disulfide	...	...	...	0.5	...	...	...	...	...	...
Tetramethylthiuram monosulfide	...	...	...	...	0.5	...	...	...	...	...
Mercaptobenzothiazole	...	...	...	...	...	...	...	...	1	...
Zinc salt of mercaptobenzothiazole	...	...	...	...	...	...	...	...	...	1
Litharge	...	...	...	...	...	3	...	...	...	...
Iron oxide	...	...	...	...	...	...	3	...	...	...
Light calcined magnesia	...	...	...	...	...	...	...	3	...	...

SERIES B

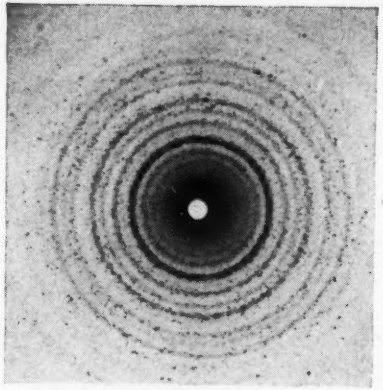
Material	B_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8	B_9	B_{10}	B_{11}
Smoked sheet	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	3	3	3	3	3	...	...	...	3	3	3
Sulfur	2	2	2	2	2	2	2	2	3	3	3
Stearic acid	1	1	1	1	1	1	1	1	1	1	1
Zinc dimethyldithiocarbamate	3	...	...	...	...	...	...	...	...	...	...
Zinc diethyldithiocarbamate	...	3	...	...	...	...	...	...	...	...	...
Tetramethylthiuram disulfide	...	...	3	...	...	3	3	3	...	...	...
Tetraethylthiuram disulfide	...	...	...	3	...	...	...	...	...	...	...
Tetramethylthiuram monosulfide	...	...	...	...	3	...	...	...	...	...	...
Mercaptobenzothiazole	...	...	...	...	...	...	...	...	5	...	...
Zinc salt of mercaptobenzothiazole	...	...	...	...	...	...	...	...	...	5	...
Benzothiazyl disulfide	...	...	...	...	...	...	...	...	...	...	5
Litharge	...	...	...	...	...	3	...	...	...	...	...
Red oxide	...	...	...	...	...	...	3	...	...	...	...
Light calcined magnesia	...	...	...	...	...	...	...	3	...	...	...

[a] The C series stocks are the same, respectively, as the B series except that no stearic acid is used in them.

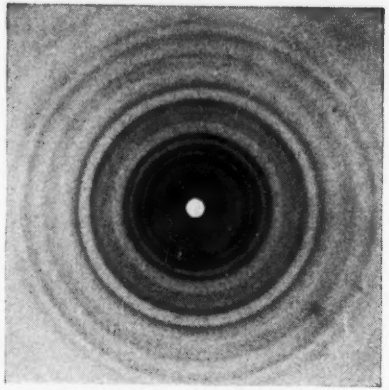
beam (pentaerythritol crystal monochromator). The patterns of tetraethylthiuram disulfide and zinc diethyldithiocarbamate are "fingerprints" of these compounds. The relative intensities for the different interferences are very different in the two. Each has intense long-spacing rings (near the center of the pattern) by which these materials may be identified in the rubber matrix. Compound A_4 (Table II) contained a very small amount of tetraethylthiuram disulfide, corresponding to its use as an accelerator in ordinary practice. The three diffraction rings at the outer edge of the pattern are due to the zinc oxide present. The characteristic lines of zinc diethyldithiocarbamate show up rather faintly in the central part of the pattern. Compound B_4 contains a much higher percentage of tetraethylthiuram disulfide than would ordinarily be used. Here the lines show up strongly. B_2 was originally compounded



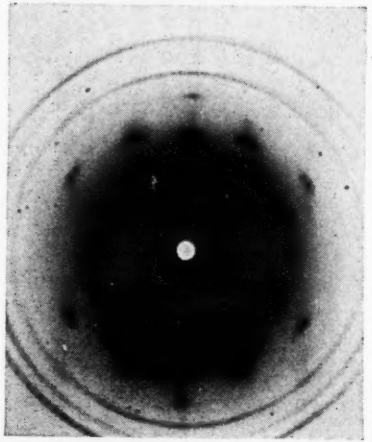
Pure stretched rubber



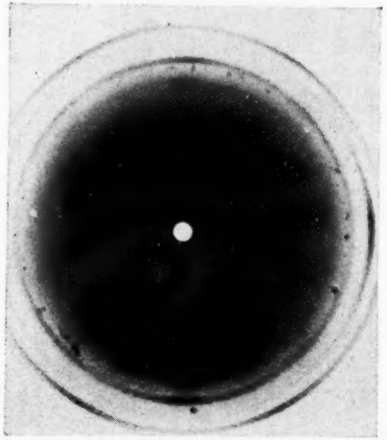
Powdered tetraethylthiuram disulfide



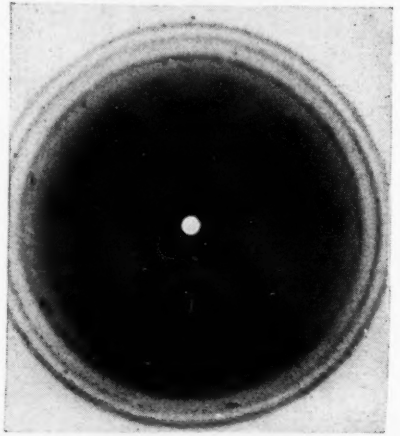
Powdered zinc diethyldithiocarbamate



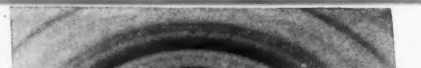
Stretched rubber stock A_4 containing nominal amount of accelerator tetraethylthiuram disulfide and zinc oxide, showing evidences of zinc diethyldithiocarbamate



Stretched rubber stock B_4, containing 3 per cent tetraethylthiuram disulfide, showing presence of zinc diethyldithiocarbamate



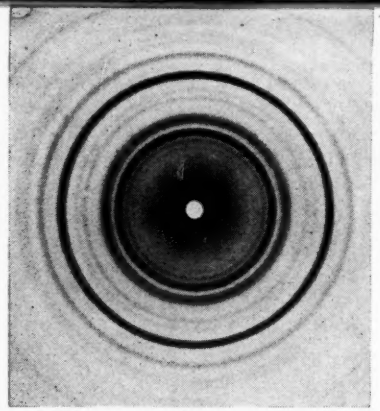
Stretched rubber stock B_2, with zinc diethyldithiocarbamate added originally



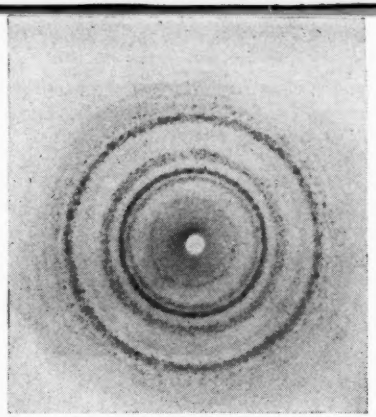
Stretched rubber stock A_4 containing nominal amount of accelerator tetraethylthiuram disulfide and zinc oxide, showing evidences of zinc diethyl-dithiocarbamate

Stretched rubber stock B_4, containing 3 per cent tetraethylthiuram disulfide, showing presence of zinc diethyldithiocarbamate

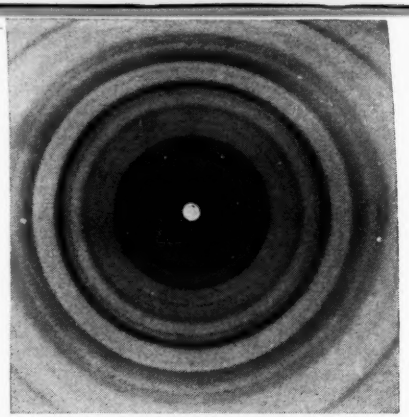
Stretched rubber stock B_2, with zinc diethyldithiocarbamate added originally



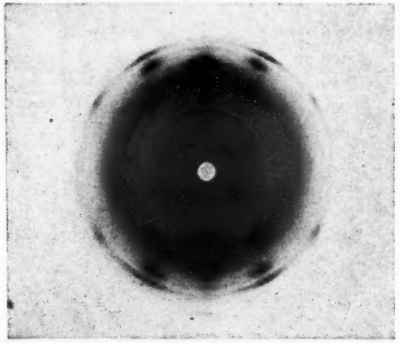
Powdered tetramethylthiuram disulfide



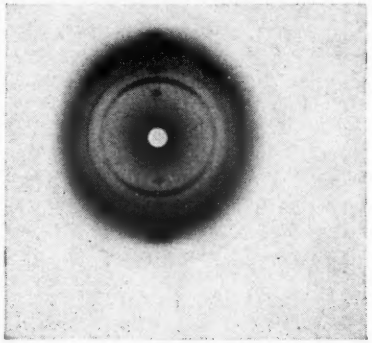
Powdered tetramethylthiuram monosulfide



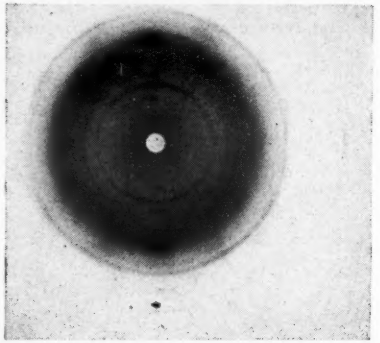
Powdered zinc dimethyldithiocarbamate



Stretched rubber stock B_3, containing tetramethylthiuram disulfide and showing presence of zinc dimethyldithiocarbamate

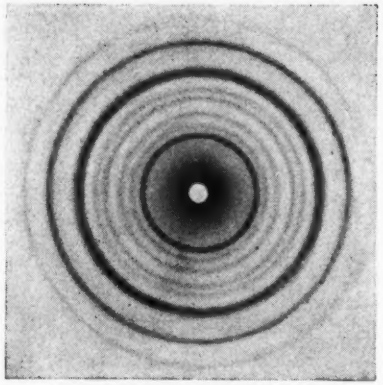


Stretched rubber stock C_5, containing tetramethylthiuram monosulfide and showing presence of zinc dimethyldithiocarbamate

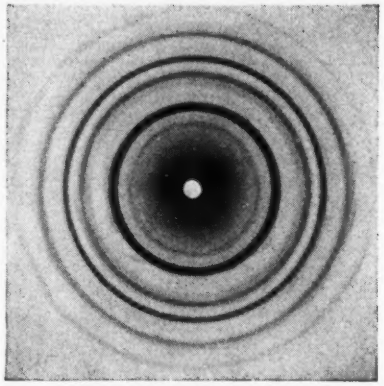


Stretched rubber stock C_1, with zinc dimethyldithiocarbamate originally added

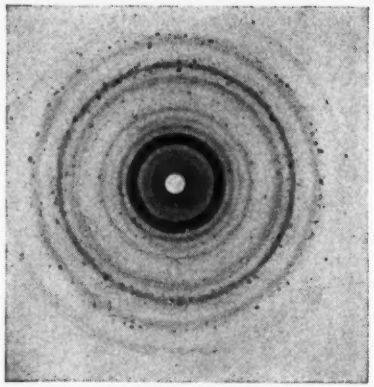
FIG. 2.—X-ray diffraction patterns of methyl derivatives.



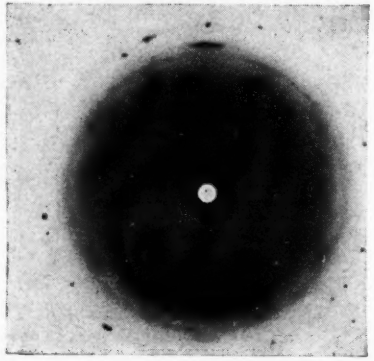
Powdered mercaptobenzothiazole



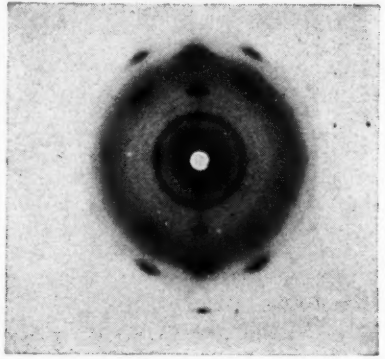
Powdered benzothiazyl disulfide



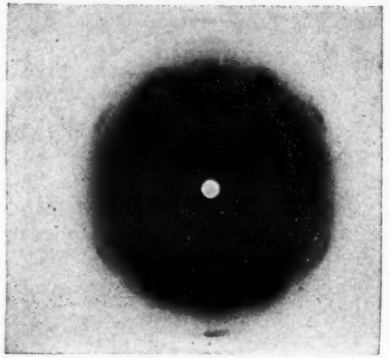
Powdered zinc salt of mercaptobenzothiazole



Stretched rubber stock C_9, containing mercaptobenzothiazole and showing presence of the zinc salt of mercaptobenzothiazole



Stretched rubber stock C_{11}, containing benzothiazyl disulfide and showing presence of the zinc salt of mercaptobenzothiazole



Stretched rubber stock C_{10} with the zinc salt of mercaptobenzothiazole originally added

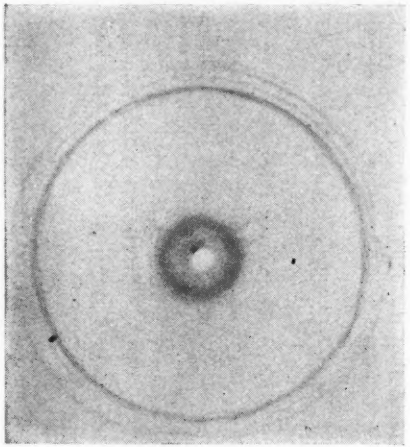
FIG. 3.—X-ray diffraction patterns of mercaptobenzothiazole family.

of mercaptobenzothiazole

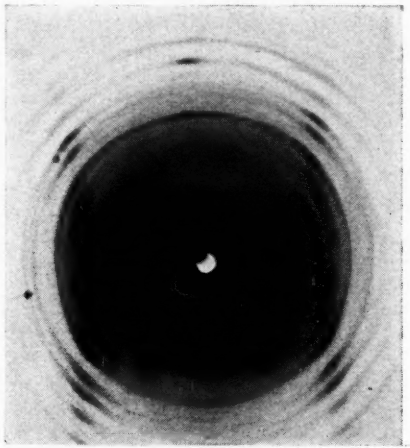
mercaptobenzothiazole

mercaptobenzothiazole originally added

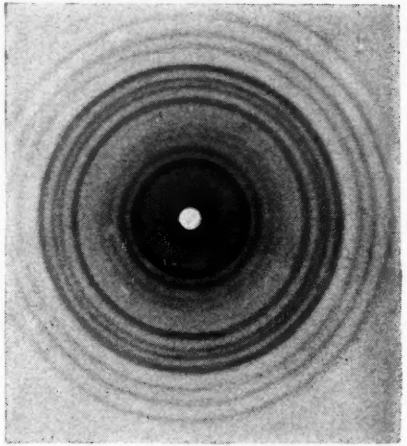
FIG. 3.—X-ray diffraction patterns of mercaptobenzothiazole family.



Powdered litharge



Stretched rubber stock B_8, containing tetramethylthiuram disulfide and lead oxide and showing presence of lead dimethyldithiocarbamate



Powdered lead dimethyldithiocarbamate

FIG. 4.—X-ray diffraction patterns of lead derivatives.

with zinc diethyldithiocarbamate as accelerator, and is shown for comparison with B_4. The patterns are identical except that the intensity of the zinc oxide lines is somewhat less in B_4, showing that much of it has been used up in the reaction to form the zinc salt of tetramethylthiuram disulfide.

Figure 2 shows the patterns for the methyl derivatives. Tetramethylthiuram monosulfide is also converted to the dithiocarbamate salt as shown in C_5. Figure 3 tells a similar story for the mercaptobenzothiazole family. The acid (mercaptobenzothiazole) and the disulfide (benzothiazyl disulfide) both react in the rubber matrix to give the zinc salt. For C_9, C_{10}, and C_{11} patterns, all three accelerators show the same product in the final vulcanizate, which corresponds to the zinc salt of mercaptobenzothiazole. The fingerprint patterns of mercaptobenzothiazole and zinc salt of mercaptobenzothiazole show that they are put into the rubber in rather large grains (specked diffraction rings). The vulcanizate patterns show uniformly small grain size, indicating that, even in the case of the zinc salt of mercaptobenzothiazole, the accelerator has melted or dissolved in the rubber matrix at the curing temperature and reprecipitated in colloidal form. Figure 4 tells the story for lead dimethyldithiocarbamate accelerator. When litharge is used with tetramethylthiuram disulfide instead of zinc oxide as an activating agent, the lead dimethyldithiocarbamate is found to be the reaction product in the cured sample.

Accelerator activators are always used with accelerators to make them work properly. Tetramethylthiuram disulfide will not vulcanize if zinc oxide is not present. It is suggested that one of the steps in activation is the chemical reaction between accelerator and accelerator activator which takes place in the rubber matrix at the curing temperature.

Examination of the C series stocks showed that the presence or absence of stearic acid had no apparent effect on these reactions.

ORIENTATION OF VARIOUS MATERIALS

Zinc dimethyldithiocarbamate is strongly oriented in the rubber matrix on stretching. This shows in the x-ray diffraction pattern by nonuniform intensity of the diffraction rings. The degree of orientation may be judged by the sharpness of the arcs into which the rings are broken. Rubber crystallites are an example of a completely oriented material. The arcs are so sharp that they appear as spots. Figure 5 shows the orientation of some of the inorganic fillers in rubber. A discussion of the orientation of these fillers is necessary to an understanding of the importance of the orientation of accelerator salts in the rubber matrix.

A dry film from latex, stretched 550 per cent (Figure 5*a*), is shown as the pattern for rubber free from all fillers. This pattern was taken at a sample film distance of 3 cm.; therefore the rubber diffraction spots appear closer to the central portion of the film than in Figures 1, 2, 3, and 4.

The sample shown in Figure 5*b* is stretched 550 per cent. Here all the rings, in addition to the rubber interferences, are due to zinc oxide. The amount of accelerator used is so small that it does not show up. These rings are not uniformly intense, as they are for the zinc oxide in a fingerprint pattern, but appear with localized intensity maxima. This means that during stretching of the rubber, the embedded zinc oxide grains are rotated and lined up in a preferred direction with respect to the direction of stretching. It is possible to calculate from the positions of the maxima on the rings the actual arrangement, with the normal to the (001) planes parallel to the fiber or stretch-

a. Pure stretched rubber

b. Stretched rubber containing zinc oxide, showing fibering of zinc oxide as well as rubber

c. Rubber stock containing Kalvan stretched 200 per cent

d. Rubber stock containing Kalvan stretched 550 per cent and showing fibering of Kalvan filler as well as rubber

e. Stretched rubber stock containing whiting

f. Stretched rubber stock containing Kalvan and iron oxide

FIG. 5.—Diffraction patterns showing orientation.

ing axis. This means, in turn, that such a powerful bond exists between the zinc oxide grains and the rubber that the rubber does not tear away from the oxide surfaces during stretching but, instead, tends to pull all the grains into parallel alignment. This is a distinctive property of the zinc oxide and, to some extent, of the compounding; for in the course of years of investigation

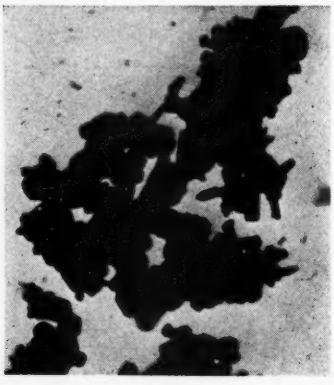


FIG. 6.—Electron photomicrograph of zinc oxide used in Figure 5*b*.

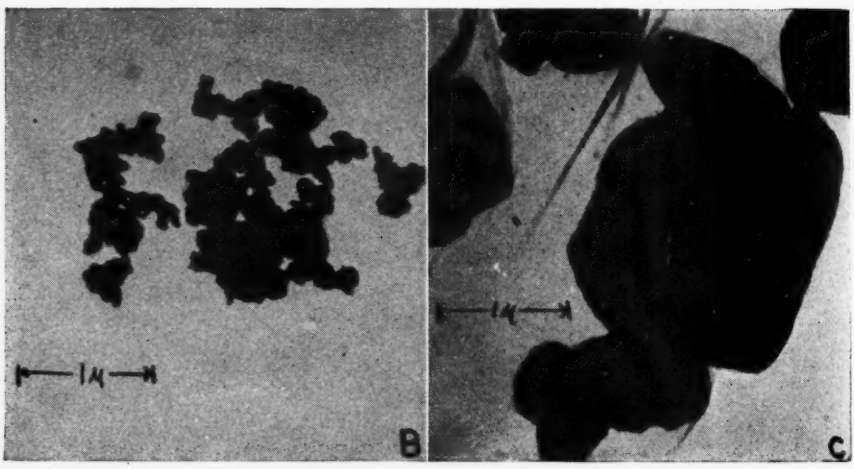


FIG. 7.—Electron photomicrographs of Kalvan (indicating primary particle size of about 300 Å.) and of whiting (*right*).

many specimens containing 5 parts of zinc oxide showed no such fibering (Katz and Bing, *Z. angew. Chem.* **38**, 439 (1925)) of these crystal grains at 550 per cent elongation.

An electron microscope picture of the zinc oxide compounded into this stock is shown in Figure 6. The individual particles are much longer in one direction than in the other two, and it may easily be understood how they would be oriented in the rubber matrix on stretching.

The stock shown in Figure 5*c* contains 25 parts of Kalvan, a finely divided calcium carbonate. Stretched only 200 per cent, the central rubber halo shows no evidence at this elongation of crystalline spots. The intense ring

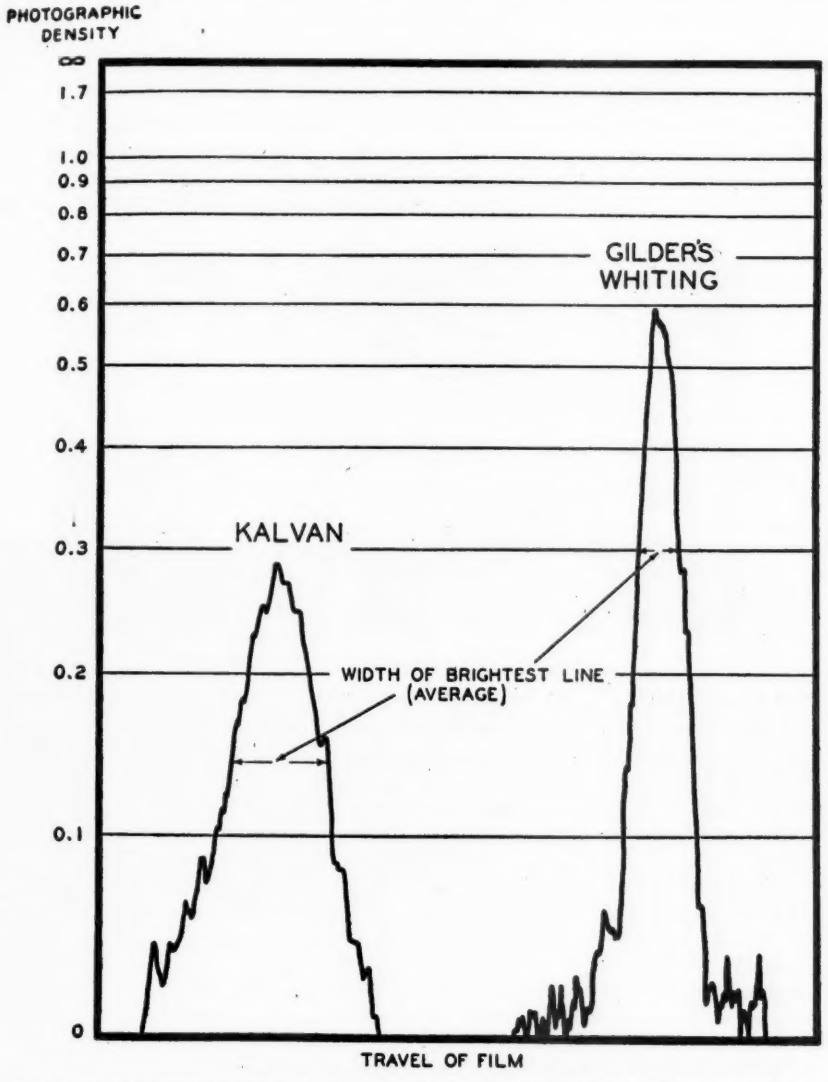


FIG. 8.—Microphotometer tracings of same calcium carbonate diffraction line in Kalvan and gilder's whiting for use in particle size determinations.

is characteristic of calcite, and all others may be identified by comparison with fingerprint patterns as belonging either to calcite or zinc oxide. The rings are continuously uniform, indicating random arrangements of all crystal grains.

Figure 5*d* represents the same stock stretched 550 per cent. Now the crystal fiber pattern for rubber has appeared; in addition the calcite lines,

especially the faint line just outside the rubber interferences and the very intense ring, show definite evidence of fibering. Again this means a remarkably powerful bond between Kalvan and rubber, and a sufficiently small size so that the grains rotate and align themselves with respect to the direction of stretch. The reverse is true as the rubber itself crystallizes, for, on release of tension, the specimen again reverts to an entirely random arrangement of rubber molecules and filler crystals. Fibering of the filler appears just when fiber spots appear for the rubber.

In Figure 5*e* the stock containing 25 parts of gilder's whiting, a coarse calcium carbonate, is stretched 550 per cent. Under these identical conditions the contrast with the preceding pattern is remarkable. The rubber crystallizes at this elongation, but the whiting crystal grains are entirely unaffected by the

FIG. 9.—Electron photomicrographs of crystals of ledate.

stretching operation, and remain in the original random arrangement. The grains are too large and the bond is too weak to permit a response to stretching deformation; the rubber must tear loose and, in a sense, flow around and past these particles like water in a stream around a fixed boulder; an exaggerated case is the same effect seen when rubber contains grains of sand. Stretching to the breaking point at about 700 per cent has no greater effect on the whiting grains.

Figure 5*f* shows a specimen containing 25 parts Kalvan and 5 parts red oxide, stretched 675 per cent. It again demonstrates the marked fibering of the Kalvan grains. Exactly the same phenomenon is shown for any specimen containing Kalvan, from 5 to 75 parts. With 75 parts of Kalvan as a common commercial proportion, fibering is prominent; but on account of the preponderance of the mineral crystals which absorb much of the x-ray energy, it is difficult to reproduce clearly the rubber interferences. Especially noteworthy is the enormous increase in tear resistance when the Kalvan content was increased from 25 to 75 parts. This is but another indication of the great capacity of the rubber to bond itself to Kalvan particles. In the stretched condition it might be expected that the resistance to tear across the fibers would be greater than parallel to them, just as it is easier to split asbestos fibers apart parallel to their length than to break a bundle across the fibers.

The differences between Kalvan and gilder's whiting have already been noted in rubber. The differences in particle size and shape of these materials

accounts for the difference in behavior. Figure 7 shows electron photomicrographs of these two materials; Figure 8 is a microphotometer tracing of the principal interference of calcite taken from x-ray patterns of these two materials for the purpose of computing particle size. Gilder's whiting is out of the range of the x-ray method. Kalvan consists of plates about 300 Å. in diameter, as shown by either the x-ray method or by direct measurement from the electron photomicrograph.

Figure 4 shows that lead dimethyldithiocarbamate is extremely highly oriented in the rubber matrix on stretching, and the layer lines even appear to be in the same position as the layer lines on the pattern for the interferences from the rubber crystallites themselves. This indicates that an extraordinarily strong bond exists between the rubber crystallites and the lead salt. A picture of this lead salt was taken under the electron microscope (Figure 9); the general shape of the material is that of long needles. Such a geometric shape would easily be completely lined up in the rubber matrix on stretching. Furthermore, these needles apparently grow or are made up from very small particles. They are clearly seen at higher magnification. Perhaps these extremely small particles account for the extraordinary bond between rubber and lead dimethyldithiocarbamate.

Tuads and its derivatives give extremely highly oriented salts in the rubber matrix on stretching. Tetramethylthiuram disulfide is frequently used in higher loadings of 3 to 5 per cent, especially in the compounding of reclaimed rubber. The presence in these stocks of considerable highly oriented salt may account for some of the desirable physical properties observed with these higher percentages. The mercaptobenzothiazole family of accelerators is not so highly oriented in the rubber matrix as the tetraalkylthiuram disulfide family.

SYNTHETIC RUBBER *

A SPECTROSCOPIC METHOD FOR ANALYSIS AND CONTROL

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Infrared spectroscopy offers methods for the identification, analysis and control of hydrocarbon mixtures which have decided advantages over physicochemical methods now in use.

Ordinary chemical methods for the analysis of mixtures of hydrocarbons are long and tedious, and the trade has long resorted to the method of physical separation of the components by fractional distillation, with identification of the components by their boiling points. This is indeed an accurate method, but is time consuming. Even though the analysis can be accomplished in a matter of hours, many hundreds of gallons of product would be produced in a plant before an error in production could be caught in the laboratory. Therefore a method of analysis which would require at most a matter of minutes and, in control, a matter of seconds, is highly desirable.

Another point for consideration is the fact that distillation requires samples in the liquid state. For the several hydrocarbons which are gases at normal temperatures, this requires condensation of the gases to obtain samples, and the usual difficulties of low-temperature distillations. The spectroscopic method, on the other hand, works equally well with gases or liquids, and requires only a very small fraction of the amount of material needed for distillation. Furthermore, this method is readily adaptable to use in the plant, since the spectrometer can be placed to allow the absorption cell to be connected into the production line. A portion of the product can be bypassed through the cell, thus obviating the necessity for transfer of samples to a separate laboratory. Lastly, the addition of a relay device permits automatic process control—a mechanical, continuous "watchman".

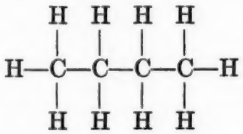
It has been pointed out many times in the literature[1] that the infrared spectrum of an organic compound is a unique property of that compound, and that, except in special instances, it retains this property on admixture with other compounds. These special instances are predictable, and are of no interest in discussing simple hydrocarbons. Thus, in general, the concentration of a given component in any particular hydrocarbon mixture can be determined by infrared measurements, if at least one absorption band of this component can be found at a wave length for which the remainder of the mixture has negligible absorption. A determination of the percentage transmission at this wave length enables one to measure the amount of this component which is present.

That the problem of spectrochemical analysis by infrared is essentially simple may be readily seen by considering the various molecules of the components as mechanical systems. The origin of infrared spectra lies in the mechanical motions of the atoms of the molecules. (Actually, of course, the origin of infrared spectra lies in the periodic variation of the dipole moment of the molecules. However, this is a complicated function and a discussion

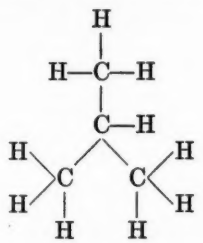
* Reprinted from *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 15, No. 2, pages 83–90, February 15, 1943.

is out of place here. It can be found in any standard text on spectroscopy.) Therefore, in discussing the mechanical analogy, we are approximating the actual spectroscopic situation, since each absorption frequency is related to a particular mechanical frequency. If we have several bodies tied together by suitable springs, and allow these masses to move freely, restrained only by the springs, they will perform certain motions with particular or characteristic frequencies. [The correlation between motions of gross bodies bound by steel springs and motions of atoms in molecules has been shown by Kettering, Shutts, and Andrews[2].] These frequencies can be made to vary by changing any of three factors—the masses involved, the strength of the springs, or the orientation of the masses.

Choosing a specific chemical compound as an example, let us take the molecule butane:

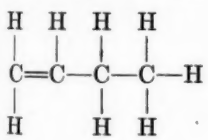


These carbon and hydrogen atoms vibrate with certain frequencies which give rise to a characteristic spectrum. If we simply rearrange this same number of atoms into another structure, we have isobutane:

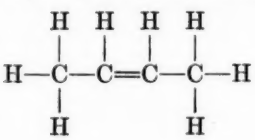


From the mechanical analogy, it may be seen that this reorientation of the masses gives rise to characteristic frequencies different from those of *n*-butane.

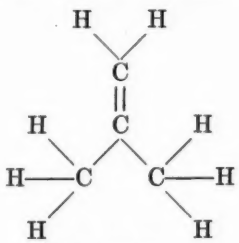
Now, if we remove two hydrogen atoms, we can form three new molecules:



Butene-1



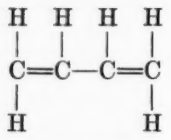
Butene-2

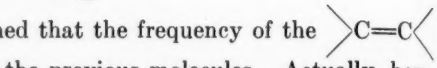


Isobutylene

The decrease in mass caused by the removal of the hydrogen atoms can be neglected, as it is only 3 per cent of the total mass. Of importance, however, is the fact that we have double the strength of one of the "springs" holding the atoms together and, hence, have a faster frequency of motion between two carbon atoms than occurs in either of the butanes. Furthermore, each of these new molecules is a mechanical system different from the other two.

Finally, by removal of two more hydrogen atoms from butene-1, we arrive at the molecule of prime interest, butadiene:



At first glance, it might be assumed that the frequency of the  spring here might be the same as in the previous molecules. Actually, however, another physical phenomenon appears, because there is a strong interaction between the motion of the carbon atoms, in this case roughly analogous to the interaction between two coupled pendulums. The organic chemist calls such molecules "conjugated" hydrocarbons or conjugated dienes, and knows that their chemical properties differ markedly from the monoolefins.

The foregoing molecules which have been chosen for purposes of illustration constitute the so-called C_4 fraction of petroleum distillations. Since they have different frequencies of motion, they give rise to characteristic infrared spectra, and so may be detected and measured quantitatively in hydrocarbon mixtures. In view of the fact, however, that the correlation between infrared absorption bands and mechanical motion holds in general, the application of this method of spectrochemical analysis is in no way limited to the cases herein cited. This method may be used in the cases of many rather subtle organic analyses, such as the differentiation of isomers, rates of oxidation, polymerization, etc.

It is the purpose of this paper to present the infrared spectra of certain compounds of particular interest in the manufacture of synthetic rubber, and to describe a method for analysis and for production control. The spectra of several synthetic rubbers are also shown.

EXPERIMENTAL

The apparatus used in this work has been described[3], together with the spectra of a large number of organic compounds and the analytical and identification techniques used.

The spectra shown in this article were obtained from an automatic recording, rock-salt prism, Littrow spectrograph. The usual working range is from 3750 cm.$^{-1}$ (2.7μ) to 750 cm.$^{-1}$ (13μ). The average spectral slit width employed decreases from 15 cm.$^{-1}$ at 3000 cm.$^{-1}$ to 5 cm.$^{-1}$ at 800 cm.$^{-1}$.

Within experimental error, all measurements made on this instrument follow Beer's law, $I/I_0 = e^{-kcx}$. Here I/I_0 is the per cent transmission (or $1 - I/I_0$, the per cent absorption) at a particular frequency, k is an absorption constant of a compound at that frequency, c is the concentration of the compound, and x is the path length used. I/I_0 is the direct experimental result measured with a spectrograph, and the accuracy with which it can be measured is determined by the characteristics of the instrument being used. Bearing this in mind, there are two pertinent considerations concerning the exponents kcx. First, except for a few special cases, at a given frequency I/I_0 remains constant as long as the product cx remains constant. Hence the concentration, *i.e.*, pressure in case of gas work, or the cell length can be chosen arbitrarily to suit experimental conditions as long as the other factor can be changed to give a suitable cx value. Secondly, if k and x are held constant, a consideration

of the exponential graph for Beer's law shows that a small error in the measurement of I/I_0 represents different absolute errors in the measurement of the concentration, depending on whether the concentration is high or low. Roughly speaking, the absolute concentration of a component can be measured more accurately when the concentration is low than when it is high. These points are elaborated below.

The spectra shown have been plotted between 2000 cm.$^{-1}$ and 750 cm.$^{-1}$, because this is generally the region from which the most information can be obtained. Results obtained outside of the region shown are discussed wherever they are of importance. These spectra are obtained from automatic recordings of the transmission through an empty and a sample-filled cell. These records are measured at given frequency intervals, and the quotient of each pair of measurements is plotted as a graph of frequency in cm.$^{-1}$ *vs.* per cent transmission. Since there may be a change in experimental conditions between these two records and since there is no attempt to take account of scattered light, the intensity scale shown is of relative but not absolute importance. However, the frequency position of the bands is accurate within the experimental error of the instrument.

Automatic recording of cell-empty, cell-filled transmissions at a given frequency for "spot" analyses is chiefly of value in measuring a long series of similar samples. Moreover, the size of the authors' recording drum limits the amount of the cell-empty transmission energy which can be used. Hence all quantitative results given in this paper were obtained by visual reading of the galvanometer spot from an auxiliary lamp and scale system.

A description of the methods of infrared spectrochemical analysis is best achieved by taking a simple example in which it is desired to obtain the concentration of one component in a mixture of known materials. The spectra of all the pure compounds in the mixture are compared, and an absorption band is chosen which is unique to the particular component of interest. Transmission measurements at the frequency of the chosen band are made on a series of known standards, in which the concentration of the one component is varied. A working calibration sheet is prepared by making a plot of concentration against these measured transmissions. Once the calibration data are obtained, any unknown may be analyzed by filling the absorption cell, measuring the percentage transmission on the instrument, and reading the answer off the work sheet—an operation requiring a very few minutes. By choosing a band unique to another component of the mixture and preparing a calibration work sheet at that frequency, two components may be measured successively. This process can be continued as long as these unique bands or combinations of such bands can be found. Working calibration sheets such as those described above have been obtained for various mixtures, and are illustrated below.

There may be some objection that this method of analysis does not make allowance for the absorption of the empty cell or for the scattered light present in the instrument. It is true that corrections for these factors could be made, and the working data could be plotted as a straight-line graph of $\log I/I_0$ against concentration. Such corrections, however, are a function of the particular instrument used, and would be of no value for analyses made on another instrument. Moreover, a working sheet on this basis would require additional calculations before it could be used. Actually, the accuracy of any analysis depends ultimately on the accuracy with which a percentage transmission can

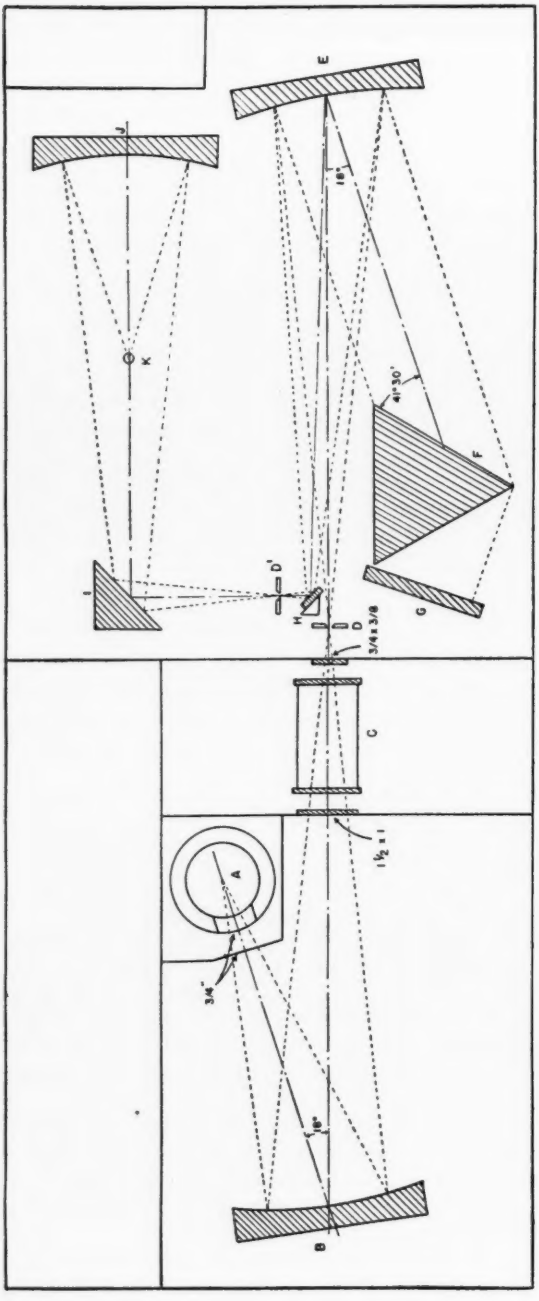


FIG. 1.—Schematic design of a compact, optically powerful instrument for making spot analyses.

Base, 10-inch channel iron.
A. Source, Nernst glower.

	Diameter (cm.)	Focal length (cm.)	Diopter
B. Spherical mirror	9	10	10
E. Spherical mirror	9	25	4
J. Spherical mirror	9	7.14	14

C. Sample cell.
D, D'. Slits.
F. 60° salt prism, 6 cm. high, 7.5-cm. base.
G. Plane mirror, 7 × 6 cm.
H. Plane mirror, 1 × 1.5 cm.
I. Prism, B. & L. 1.25-inch glass.
K. Thermocouple.

be measured, and the computational step from this measurement to concentration analysis should be as short as possible.

Because of the persistent requests for suggestions concerning infrared apparatus, the authors have designed in this laboratory a small, very simple

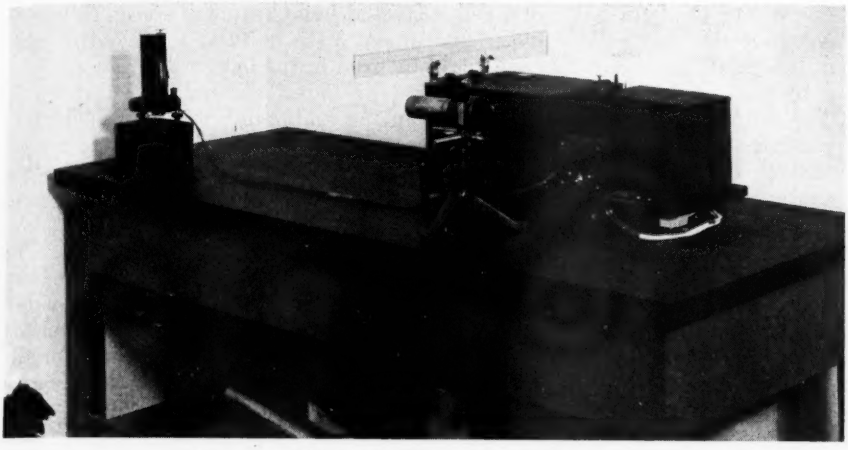


FIG. 2.—Small infrared spectrometer for spot analyses.

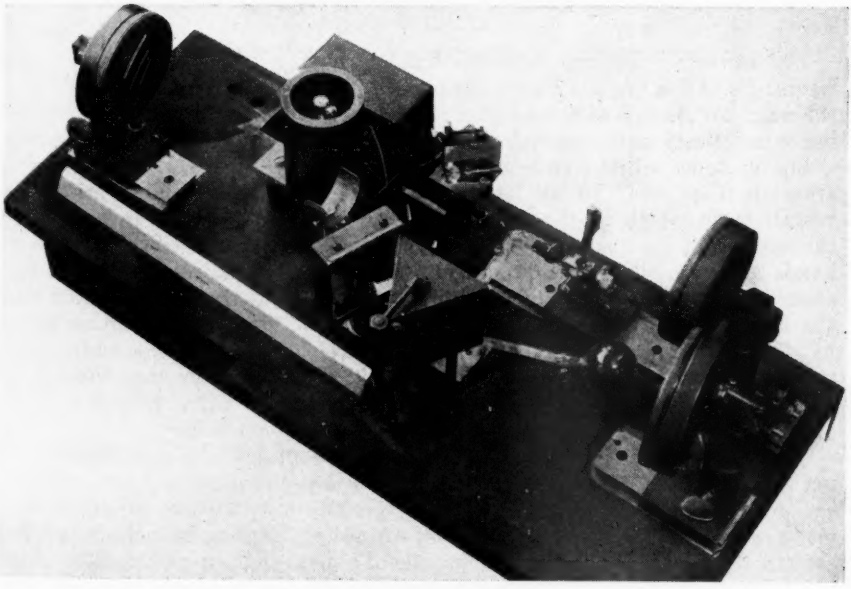


FIG. 3.—Small infrared spectrometer with covers removed.

spectrometer with sufficient resolution and optical power to satisfy the demands of the problems at hand. This instrument was built by the Porocel Corporation, and is now in very satisfactory service for hydrocarbon analyses at their plant.

A schematic diagram of the spectrometer is shown in Figure 1. The light path through the instrument is shown in dotted line. The instrument has an aperture of f. 3.5, and the slits are adjustable to give the combination of energy and resolution desired for a given analysis. The design is a typical 60° rock-salt prism Littrow mounting. In its present use, the absorption cell is introduced into the light path on a cell way, and hand readings are made from a galvanometer and scale. If the instrument is to be used as a control relay in the plant, the absorption cell could be fixed in the light path, and gas from a by-pass in the production line would be blown continuously through it. The introduction of a suitable device in the amplifying system would make possible the opening and closing of valves, variation in heat input in the process control, or the sounding of alarms. The instrument may be used for the analysis of liquid or solution samples merely by introducing a suitable absorption cell in the light path.

A photograph of the completed spectrometer is shown in Figure 2. The apparatus is shown from the operator's viewpoint, with the galvanometer lamp and scale used in making analyses. The two glass leads to the absorption cell can be seen projecting above the instrument. Figure 3 shows the completed spectrometer with the covers removed and a foot rule laid on the base for size comparisons. This view is directly comparable with the schematic diagram of Figure 1, so the component parts may be determined by corresponding positions on the base. The performance of this small spectrometer with respect to optical power, resolution and reproducibility far exceeded expectations at the time it was designed.

DISCUSSION

An infrared spectrum may be divided roughly into two parts, a high-frequency and a low-frequency region, the division line being somewhere in the neighborhood of 1300 cm.$^{-1}$. In the high region, the observed absorption bands are likely to be caused essentially by a vibration of a specific pair or group of atoms within a molecule, such as O—H, C—H, N—H, C=O, C=C, aromatic rings, etc. In the low region, on the other hand, bands arise from vibrations in which all the atoms of the molecule take part. In comparing the spectra of an unknown and a known molecule, complete coincidence of bands both in position and intensity in the high region indicates that the same atomic groups are present, but does not necessarily justify the conclusion that the molecules are identical. On the other hand, since the lower-frequency bands are more nearly characteristic of the molecule as a whole, a matching of their spectra throughout both regions would certainly show that the known and unknown molecules are identical. These characteristics, as well as their use in analytical work, are illustrated in the discussion below.

Figure 4 shows the spectra of *n*-butane, isobutane, and a mixture of 36 per cent *n*-butane, 60 per cent isobutane, and 4 per cent other gaseous hydrocarbons. Both spectra of the pure compounds have strong bands at 1450 cm.$^{-1}$, a general C—H group bending vibration. Again, both have a band around 1375 cm.$^{-1}$ which is characteristic of a methyl group absorption. This band in isobutane is double—one component at 1375 cm.$^{-1}$, the other at 1360 cm.$^{-1}$. This doubling is characteristic of a terminal isopropyl group.

However, spectral differences and not similarities are of prime importance in analytical work. It is immediately evident that *n*-butane has a strong band at 975 cm.$^{-1}$, a region in which there is negligible absorption in isobutane. The reverse situation is true at 1180 cm.$^{-1}$, where the iso form has a band and

the normal has not. Both these bands are seen to appear in the mixture. Therefore, an analysis for one component in the presence of the other is a simple matter according to the technique outlined above. The working calibration sheet shown in Figure 5 was obtained by setting the instrument for the isobutane band at 1180 cm.$^{-1}$, filling an absorption cell with mercury manometric measures of isobutane, making up the mixtures with *n*-butane to about 150-cc. total pressure, and determining the percentage transmission of the prepared samples. A smooth curve drawn through these points shows a scattering of less than ± 1 mm. of isobutane, or an accuracy of better than ± 1 per

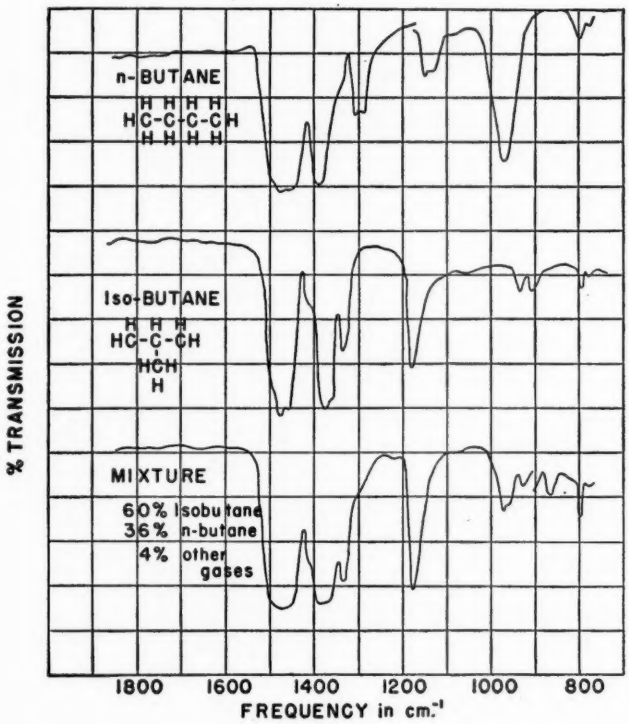


FIG. 4.—Infrared spectra of pure and mixed C_4 saturated hydrocarbons.

cent of the total mixture, in spite of the rough method of filling the cell. The time to obtain this curve was 3 hours. After this working sheet is once obtained, the time to analyze any unknown after the cell is filled is no more than 5 minutes. If the *n*-butane content is desired, another 5 minutes is required for a measurement at 975 cm.$^{-1}$. Incidentally, it is not essential in an analysis that one component have a negligible absorption at the frequency for which the second absorbs strongly. Actually, the accuracy of analysis at any frequency is a linear function of the difference in absorption coefficients (k) of the two components at this frequency. To make this difference as large as possible, analyses are made at that frequency for which one component has a strong absorption while that of the other is negligible.

To illustrate the method of working with a log percentage transmission plot, the values of Figure 5 were corrected by a constant factor for scattered light, cell-window absorption, and variation in total pressure; and the straight-line graph of Figure 6 was plotted. This method of treating the data is theoretically much more rigorous. The resultant accuracy (or point scattering) is the same in Figure 6 as in Figure 5, although a greater time is required to prepare the calibration sheet. However, the method of log I/I_0 plotting is useful for extrapolation to a range of concentration for which calibration standards might be difficult to procure.

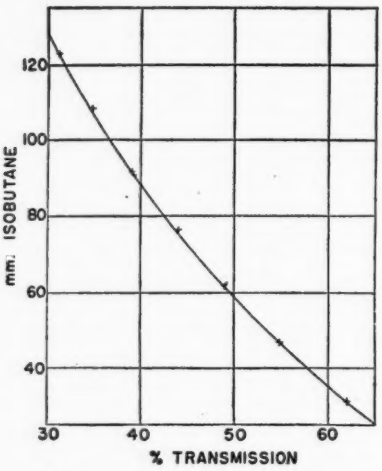


FIG. 5.—Working calibration curve at 1180 cm.$^{-1}$
Percentage transmission of various pressures of isobutane in a mixture of approximately 150 mm. of butane + isobutane. Scattering of points is less than 1 mm. in 150, or an accuracy of better than ±1% of total composition.

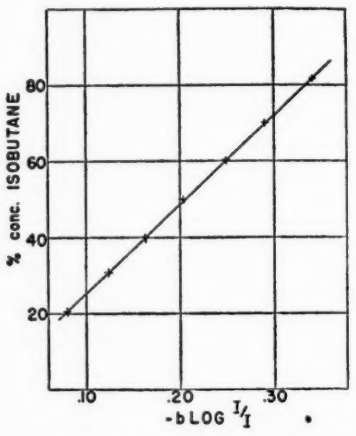


FIG. 6.—Graph of Figure 5 reduced to a straight-line plot of log percentage transmission *vs.* isobutane concentration.
Values of Figure 6 have been corrected for scattered light and variation in total pressure. Constant *b* includes cell length, total pressure, and absorption coefficient *K*.

With respect to this particular mixture, the authors measured some samples for their isobutane content to compare results with those obtained by fractional distillation. Here one sample was taken as a standard and the method of

TABLE I

ISOBUTANE CONTENT

Chemical (percentage)	Spectroscopic (percentage)
38.3	38.3 (standard)
20.8	21.3
0.0	0.26
43.9	42.7
48.8	48.7

Figure 6 was used for measuring the others. Table I gives the results for each method of analysis. This comparison offers further proof of the accuracy of spectroscopic methods.

Figure 7 shows the spectra of the unsaturated C_4 hydrocarbons. It was pointed out above that a double bond would be a much stronger "spring" than a single bond. This stronger spring is apparent in 1-butene, 2-butene, and

isobutylene, where a C=C vibration occurs at 1650 cm.$^{-1}$. In butadiene, however, the presence of two strong springs connected by a weaker one causes two strong bands, one at 1825 cm.$^{-1}$, the other at 1600 cm.$^{-1}$. The 1-butene was rated at 95 per cent purity. Because of the presence of the weak bands at 1825 cm.$^{-1}$ and 1600 cm.$^{-1}$, it is likely that butadiene is a major impurity in 1-butene.

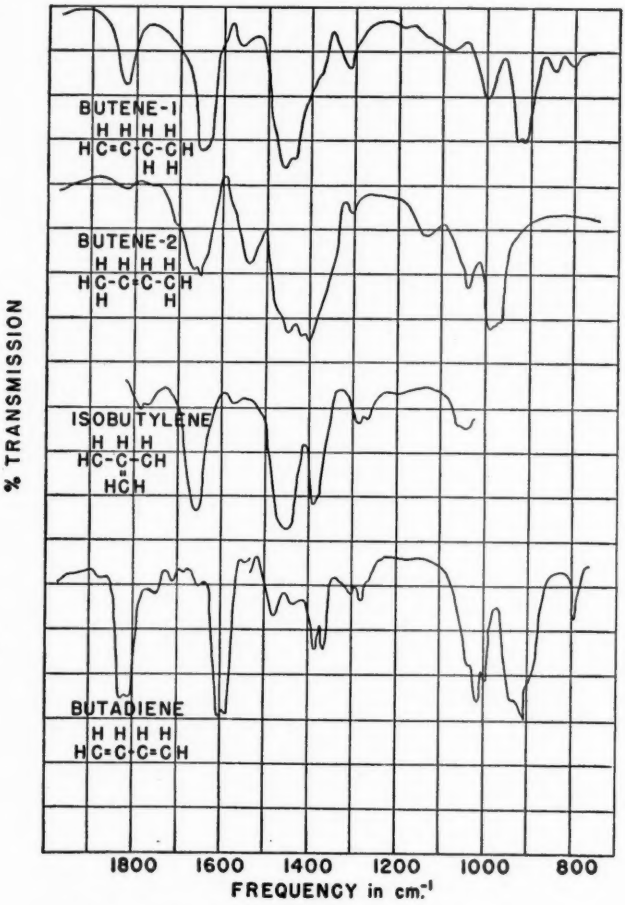


FIG. 7.—Infrared spectra of C_4 unsaturated hydrocarbons.

These higher-frequency absorptions can be used in analyzing unsaturated hydrocarbons for the presence of saturated components, or monoölefins for the presence of conjugated olefins. The spectra of such mixtures are shown in Figure 8. Figures 9 and 10 are working sheets prepared for a series of mixtures of 1-butene in *n*-butane, and butadiene in 2-butene. Again, the scattering of these points shows that the accuracy of analysis for one component in this range is better than ±1 per cent of the total mixture.

The authors have tried to illustrate the applicability of infrared spectroscopic analysis to the essential steps in the preparation of butadiene for rubber synthesis. There are two further considerations which should be discussed.

It is evident from the examples chosen that the contents of the binary mixtures shown above can be analyzed quickly and accurately. The question may arise as to the possibility of a complete analysis of a mixture of all C_4 hydrocarbons which may result from one process. The success of such an

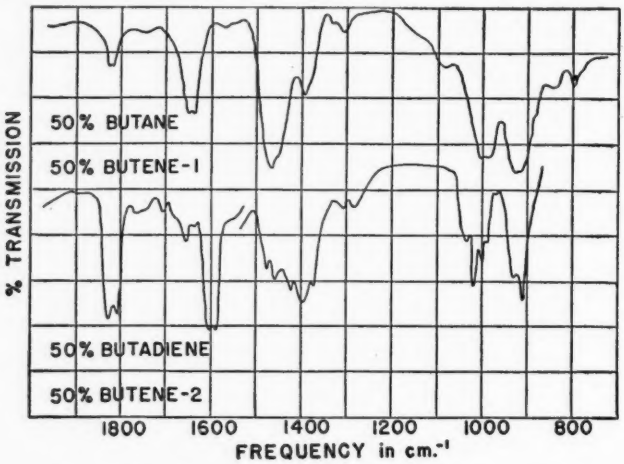


FIG. 8.—Infrared spectra of mixed unsaturated C_4 hydrocarbons.

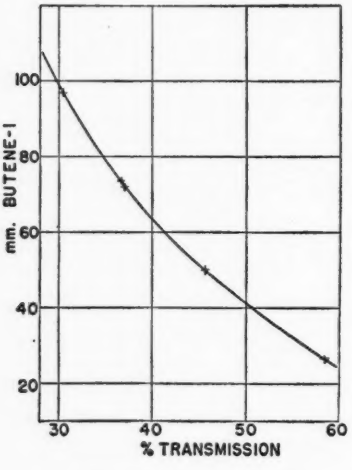


FIG. 9.—Working calibration curve at 1650 cm.$^{-1}$
For partial pressure of 1-butene in approximately 120 mm. of 1-butene + *n*-butane.

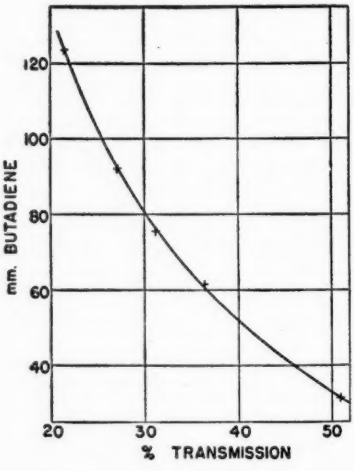


FIG. 10.—Working calibration curve at 1825 cm.$^{-1}$
For partial pressure of butadiene in approximately 150 mm. of butadiene + 2-butene.

analysis cannot be predicted from an examination of the spectra shown. It may not be possible to find a band for each component which is unique to that component. However, there is the possibility of finding a band which is common to two components and a band unique to one of these two. The second component can then be found by a difference method. An extension

of this method may lead to the necessity of allowing for three or four components at one frequency. Such a situation may tend to lower the overall accuracy of the analysis to a slight extent. However, this method can be used without appreciable loss of time. In fact, a routine analysis performed in this laboratory measures the presence of six impurities in a mixture with an accuracy of ±1 per cent of the total mixture.

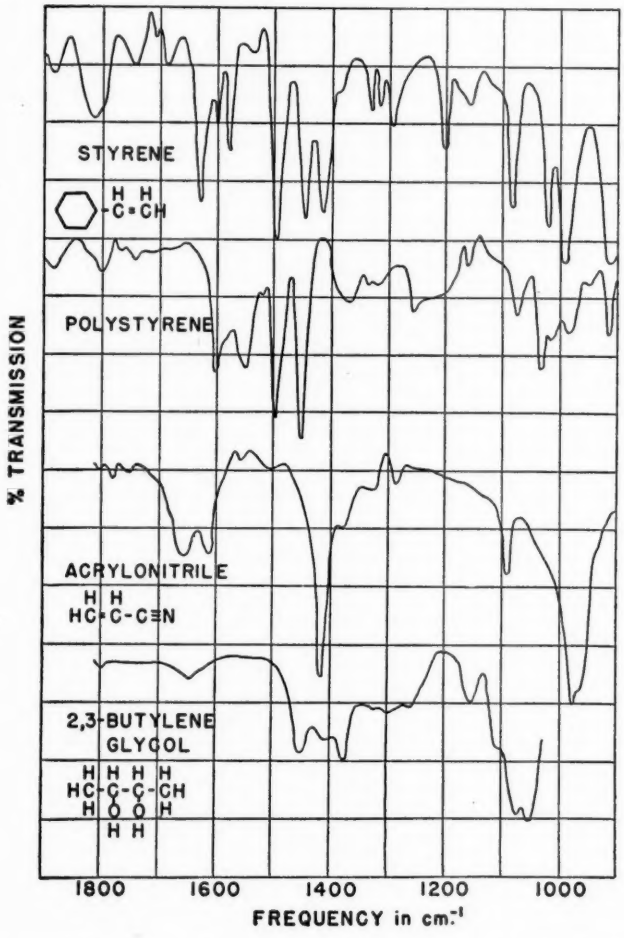


FIG. 11.—Infrared spectra or some intermediates in production of synthetic rubber. Samples studied as liquid or solid films.

The second point concerns the fact that the working sheets shown measure the presence of one component between 20 and 80 per cent concentration. It can be seen from the steepening slope above 80 per cent concentration, or from a consideration of the exponential nature of Beer's law, that the accuracy of direct analysis for one component falls off as the concentration of that component approaches 100 per cent. In fact, for such high concentrations it is more accurate to analyze for the lesser components and obtain the major

component by difference. Below 20 per cent, the accuracy of analysis for a component increases markedly. Consider an analysis at 1180 cm.$^{-1}$ for a 1 per cent concentration of isobutane in *n*-butane. Since the absorption of *n*-butane is practically negligible, the absorption cell can be filled to atmospheric pressure. Isobutane will be present to 7.6-mm. pressure and can be measured with an accuracy better than ±1 mm. Hence the accuracy for this concentration of

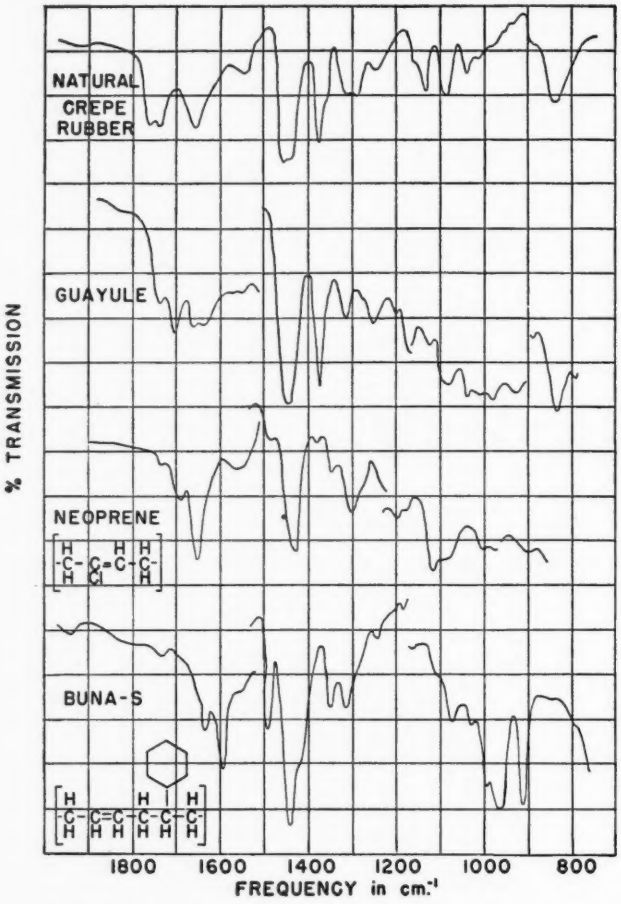


FIG. 12.—Infrared spectra of natural and synthetic rubbers.

isobutane is better than 1 part in 760 or approximately ±0.1 per cent of the total mixture.

The infrared spectra of a few other intermediates in the production of synthetic rubber are shown in Figure 11. The spectrum of polystyrene has been included to illustrate the spectral changes which occur on polymerization. The monomer styrene bands at 1625 cm.$^{-1}$, the C=C vibration, and at 1410 cm.$^{-1}$, the bending vibration of the vinyl C=H group, have completely disappeared in the polymer. These unique bands are of great value in measuring the amount of monomer present in a monomer-polymer mixture. By extract-

ing time-interval samples from a polymerization reaction, the rate of reaction under various experimental conditions can be measured quickly and accurately. The method suggests itself as a possibility for measuring reaction rates in rubber synthesis. A characteristic band of acrylonitrile is the C≡N absorption at 2240 cm.$^{-1}$ (this region is not shown in Figure 12). Since this chemical group is not affected in the synthesis of Perbunan and Hycar, it reappears in

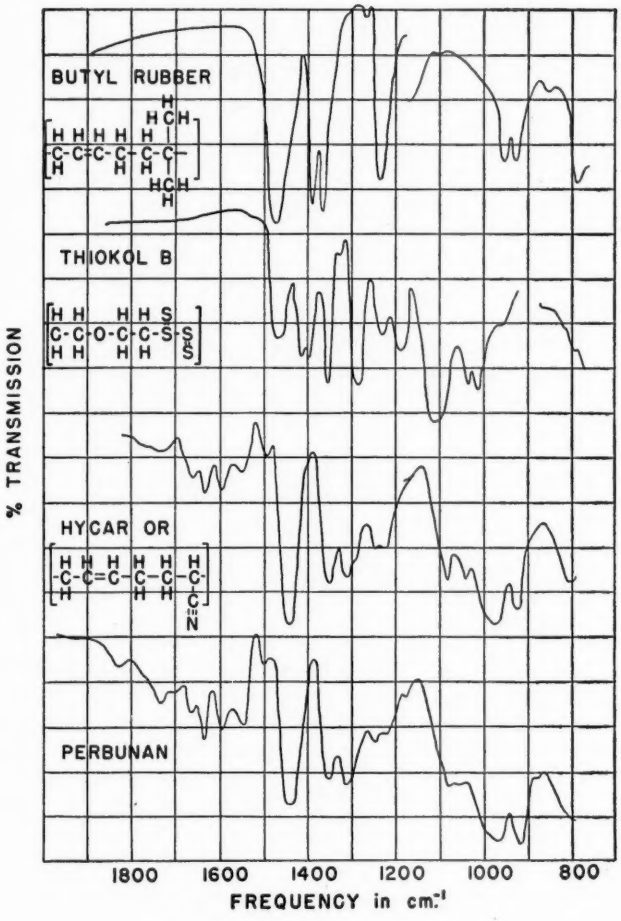


FIG. 13.—Infrared spectra of synthetic rubbers.

the spectra of these rubbers. Again a unique band is offered for quantitative work. The spectrum of 2,3-butyleneglycol shows little absorption in the unsaturated region from 1900 cm.$^{-1}$ to 1600 cm.$^{-1}$. An analysis of unsaturated materials in this compound is, therefore, readily possible.

To show that infrared spectroscopy can be used also to derive information concerning some natural and synthetic rubbers themselves, several spectra are shown in Figures 12 and 13 (the formulas for the unit structure of these compounds were taken from Powers[4]).

These spectra exhibit marked differences, so that an unknown rubber can be identified by comparison of its spectrum with that of a known sample. Moreover, the spectra offer information concerning the structure of the molecules themselves.

These samples of rubber were the purest ones available to the authors at the time. Their history is not well known, and some oxidation which would lead to the presence of spurious bands in the spectrum may have occurred. The general spectrum, however, must be close to that of the pure substance. The method of preparing samples for study was to form a "gluey" state of the rubber by mixture with a suitable material such as carbon tetrachloride or acetylene tetrachloride. A film of this glue was spread on a rock-salt plate, and the solvent was evaporated.

Strong bands are observed in the spectrum of pure natural crepe rubber at 1750 cm.$^{-1}$, 1610 cm.$^{-1}$, and 1375 cm.$^{-1}$. It was known that this sample was 6 years old. This fact is evident in the spectrum, for the C=O band at 1750 cm.$^{-1}$ shows that considerable oxidation has taken place. The strength of this band could be used to make a quantitative analysis of the amount of oxidation in a sample for correlation with elasticity or abrasion tests. The 1610 cm.$^{-1}$ band is probably caused by a C=C bond; the 1375 cm.$^{-1}$ absorption points to the presence of methyl linkages. The small shoulder at 1360 cm.$^{-1}$ suggests that some of these may be terminal isopropyl groups. Somewhat similar bands are seen in the spectrum of guayule, although the greater number of absorptions in the region from 1600 cm.$^{-1}$ to 1800 cm.$^{-1}$ points to a greater complexity of unsaturated material in the guayule than in the crepe rubber.

The bands at 1650 cm.$^{-1}$ in Neoprene-GN and at 1635 cm.$^{-1}$ in Buna-S are caused by the presence of the C=C linkage. Neither compound has indication of methyl groups at 1375 cm.$^{-1}$. Butyl rubber and Thiokol-B show no absorption in the 1650 cm.$^{-1}$ region, suggesting that there is far less unsaturation in these samples than in the previous two. Butyl rubber has a peculiar double band at 1375 cm.$^{-1}$. This band splitting is different from that exhibited by an isopropyl group, and may be characteristic of a tertiary butyl group. The bands at 1595 and 1495 cm.$^{-1}$ observed in Buna-S are characteristic of an aromatic ring. The presence of these bands in an unknown rubber sample would immediately label it as a styrene-type rubber. The spectra of Perbunan and Hycar-OR are seen to be very similar in frequency absorption, although the relative intensities of the bands are different. This similarity is not surprising, since Perbunan is approximately 25 per cent acrylonitrile and 75 per cent butadiene, while the ratio is 40 per cent to 60 per cent in Hycar. The strong 1825 cm.$^{-1}$ band of butadiene has disappeared, since the conjugation has been broken in synthesis. As pointed out above, these two spectra show the C≡N band at 2240 cm.$^{-1}$, which provides an immediate tag for acrylonitrile rubbers.

SUMMARY

Rapid quantitative analysis of compounds of prime interest in the production of synthetic rubber is possible by a relatively simple technique of spectroscopy. An apparatus suitable for such analyses is described, which does not require skilled technicians. It may be easily converted into an automatic control device for the control of production. The spectra of the natural and synthetic rubbers illustrated provide information concerning the structure of

rubber molecules and can be used to identify the type of rubber present in unknown samples.

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THE ROLE OF ZINC OXIDE IN COMPOUNDING GOVERNMENT SYNTHETIC RUBBER *

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St. Joseph Lead Co., Monaca, Pennsylvania

The nation's crude rubber supply is diminishing at such a rapid rate that the construction of large heavy-duty high-speed tires of 100 per cent synthetic rubber for the Army and Navy is of paramount importance. Past experience in natural rubber with solid tires and bus balloon tires containing high loadings of zinc oxide indicates the value of zinc oxide for this type of service. Because of the much higher heat generation during flexing of butadiene-styrene copolymer rubber compared with natural rubber, the role of zinc oxide in producing cool-running GR-S treads and carcasses should be of greater importance than ever. This would not be the case, however, if the decision were to be based on laboratory flexometer tests as run in the past. It is the purpose of this work first to point out why laboratory flexometers have failed in this respect, and to describe a modified type of flexometer test, using the St. Joseph Lead Co.'s machine[1] (see Figure 1) which, we feel, should more nearly duplicate road tests on this type of compound, and then to present data, using this type of test, which indicate that mixtures of channel black with zinc oxide give higher tensile strength and cooler running stocks than those containing soft blacks or mixtures of soft blacks with channel blacks.

ROAD *VS.* LABORATORY FLEXOMETER TESTS

The crux of the situation lies in the fact that the service conditions of a tire are such that the heat conductivity of the stock aids in the dissipation of heat which is generated. That is, the greater the thermal conductivity of the stock, the lower the running temperature. This is especially true of the tread compound and, to a lesser extent, the carcass, whose generated heat must be conducted through itself, the tread, and sidewalls. In the laboratory flexometer, the testing conditions are such that the thermal conductivity and diffusivity of the sample play a minor role in dissipating the heat generated. This condition is brought about by the fact that the laboratory sample is thick in relation to the area exposed for radiation cooling [less than 1/550 that of a tire (see Appendix 1-c)] and, furthermore, by the fact that it is tested between insulated face-plates such as wood, hard rubber, or micarta, and there is little or no chance for heat dissipation. Other factors of equal importance are high peripheral speed of the tire (35 m.p.h. if the car is traveling 35 m.p.h.) compared to the laboratory test-specimen of 3.9 m.p.h. peripheral speed (see Appendix 2-b), and the fact that a tire on a car traveling 35 m.p.h. is not only rotating around the axle, but is moving horizontally through the air with a 35 m.p.h. speed, which is the equivalent of a 35 m.p.h. cooling wind, neglecting tread wind drag, blowing across it.

One other fact which tends to confirm the conclusion that the laboratory flexometer, as normally run with thermally insulated face-plates, measures mainly heat generation is that the work done on the sample is only slightly temperature attained during test. This indicates that most of the work done on the sample is converted to heat. Very little of this is lost during a test. greater than that calculated from thermal data to bring the sample up to the

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DEVELOPMENT OF NEW TEST METHOD

To bring into the flexometer test the effect of thermal conductivity of the stock so as to simulate more nearly road conditions, it was felt that the ratio of radiating surface to thickness of the sample must be increased to be more nearly that of a tire and allow more heat flow. Consequently tests were run in which ¼-inch of the bakelite face-plate of the flexometer was removed and replaced with a ¼-inch steel plate. Comparative tests were then run between

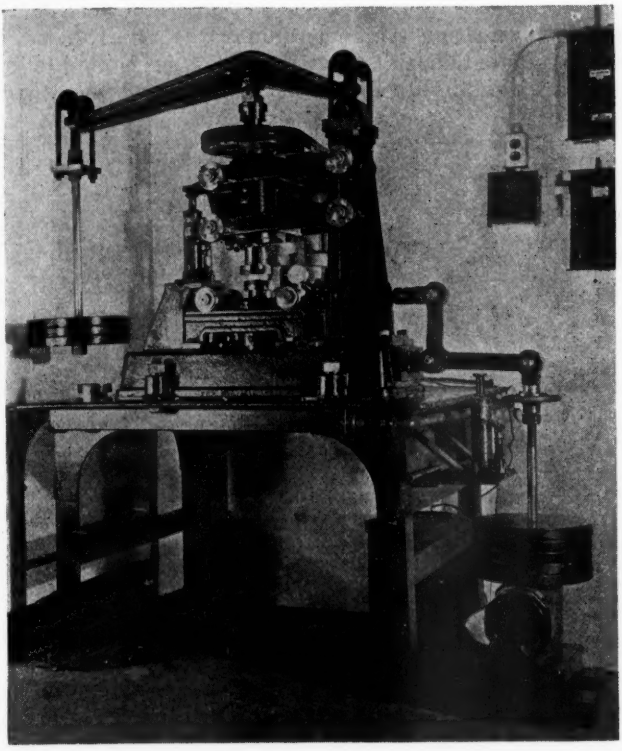

FIG. 1.—St. Joseph Lead Co.'s flexometer.

a semireënforcing furnace black stock and a high zinc oxide stock. For these tests, compound E 1037 (see below), which contained 30 volumes of pigment on 100 parts by weight of GR-S (Buna-S) was used. The cure was 60 minutes at 292° F for compounds 537 J (zinc oxide) and 538 J (furnace black).

E 1037 BASIC

	Parts by weight	
GR-S (Buna-S)	100.	
Sulfur	2.5	
Mercaptobenzothiazole	1.5	
Zinc oxide	5.0	
Stearic acid	2.5	
B.R.T. No. 7	1.0	
Pigment*		30 volumes

* Parts by weight of pigment = 30 × sp. gr. of pigment.

The results were so surprising that further tests were run, using ¼-inch metal plates on both face-plates. A high-speed blower was then installed to blow cooling air past the sample. The air velocity was adjusted to 32.4 m.p.h., using a Variac to vary the blower speed and a Velometer to measure the air velocity at the sample. In all these tests, standard cylindrical test-specimens 1½ inches in diameter and 1½ inches in height were run, with a vertical load of 485 pounds and a horizontal deflection of 0.130 inch. The temperature at the center of the test-specimen was measured with a hyponeedle thermocouple at the end of 40 minutes of test. This 40-minute temperature was taken as the criterion for evaluating the cool running properties of the stocks. In Figure 2 the 40-minute temperature values have been plotted for a 30-volume furnace black stock and a 30-volume zinc oxide stock, using regular bakelite

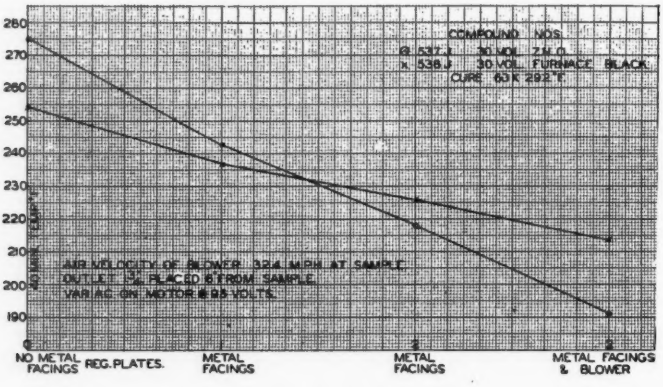
COMPOUND NOS.
30 VOL. ZN O.
30 VOL. FURNACE BLACK
CURE 60 @ 292°F.
AIR VELOCITY OF BLOWER 32.4 M.P.H. AT SAMPLE
VARIAC ON MOTOR @ 95 VOLTS.
NO METAL FACINGS REG. PLATES.
METAL FACINGS
METAL FACINGS
METAL FACINGS & BLOWER

FIG. 2.—The effect of heat conductivity of pigment on temperature developed in sample and the effect of conditions of heat radiation on temperature developed in sample. Comparison of zinc oxide and furnace black with different-type face-plates.

insulating plates, one ¼-inch metal-faced lower plate, two ¼-inch metal-faced plates, and two ¼-inch metal-faced plates with the blower. The results are self-explanatory and show that, using insulating plates such as are used in the ordinary flexometer test, furnace black generates less heat than zinc oxide. When the two metal-faced plates are used, however, the zinc oxide stock is cooler running than the furnace black stock and, with the addition of the blower, the zinc oxide stock is considerably cooler (23° F) than the furnace black compound.

Although we do not know the exact point on this graph (Figure 2) where tire road tests would fall, we do feel, after careful consideration of all known factors involved, that it would be toward the right side of the graph. Consequently further tests shown in this paper were run, using the two metal face-plates and no blower (Figures 3, 4, 5 and 6). It might be pointed out here that these tests indicate that, if high heat-conductive pigments are used in tread and carcass, and proper attention to tire design is given (to take advantage of these thermal effects), a cooler running tire might be made, with resulting longer life. The tread design, tread thickness, lettering on sidewall, etc., all affect the air friction and aid flow conditions, which in turn affect cooling of the tire. Even fender design may be an important factor.

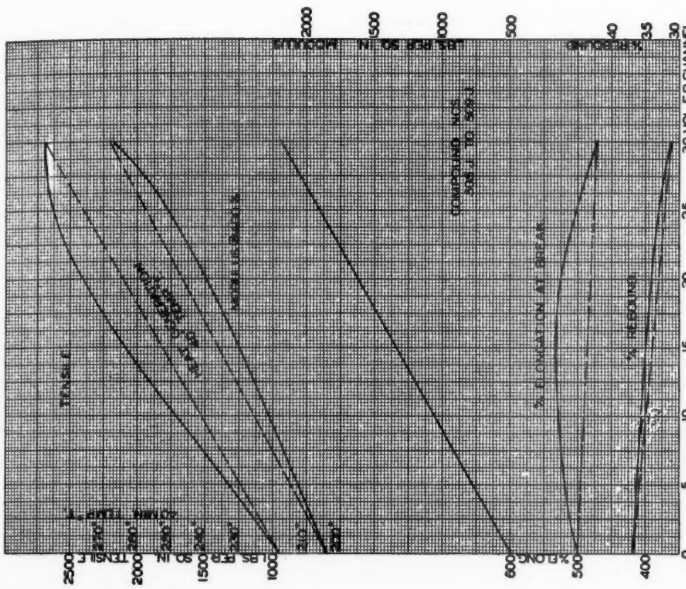

FIG. 4.—Heat generation and physical properties—no. 42 zinc oxide, easy-processing channel black blends (actual results ————; calculated results - - - - - -).

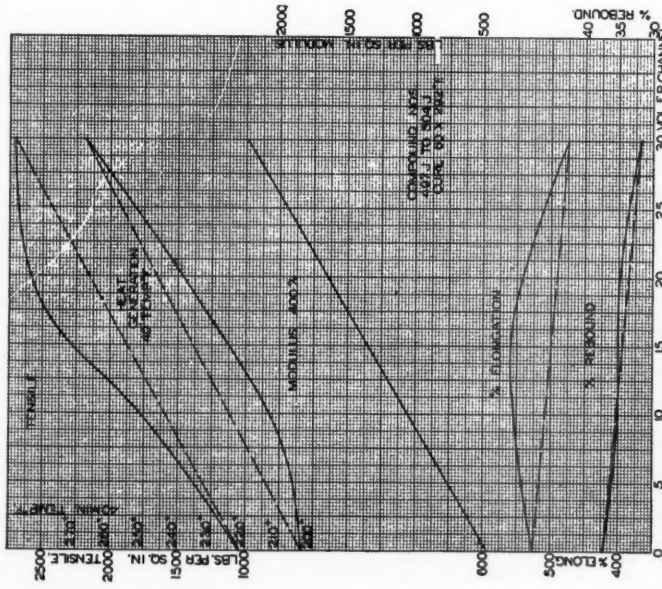

FIG. 3.—Heat generation and physical properties—no. 20 zinc oxide, easy-processing channel black blends (actual results ————; calculated results - - - - - -).

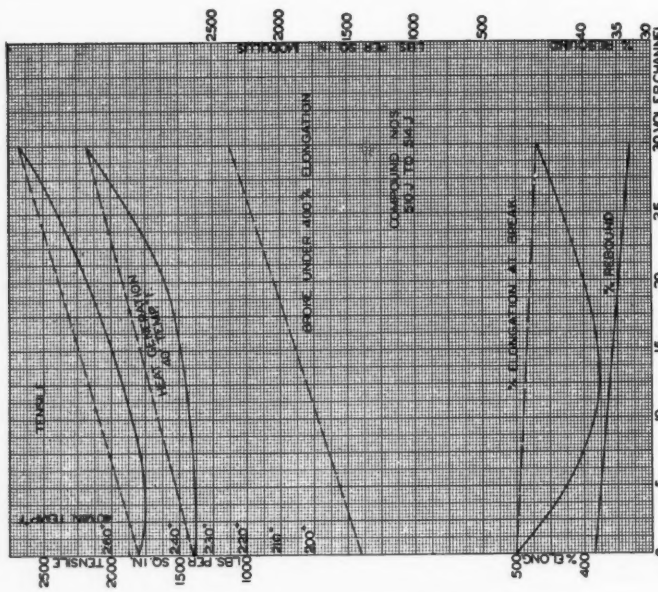

FIG. 6.—Heat generation and physical properties—furnace black, easy-processing channel black blends (actual results ————; calculated results - - - - - -).

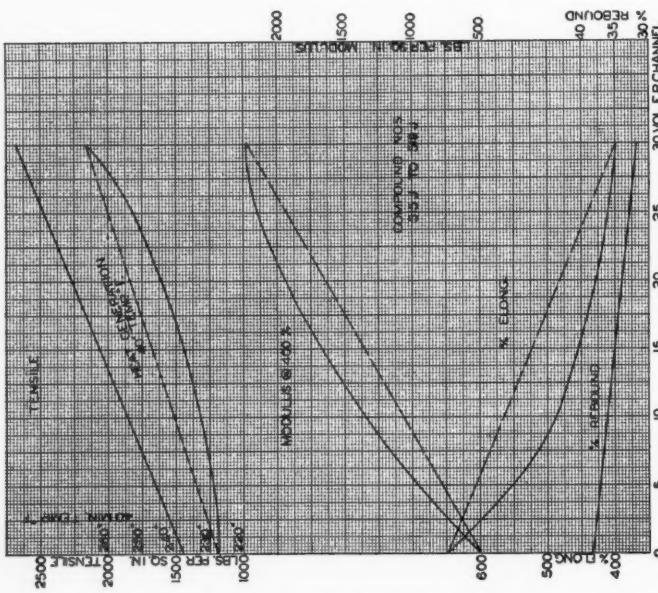

FIG. 5.—Heat generation and physical properties—fine thermatomic, easy-processing channel black blends (actual results ————; calculated results - - - - - -).

STUDY OF VARIOUS PIGMENT BLENDS

Easy-processing channel black-zinc oxide.—Since in GR-S (Buna-S), zinc oxide by itself gives low tensile stocks having relatively low heat generation and high heat conductivity, whereas channel black stocks give high tensile strength, high heat generation, and low thermal conductivity, it was felt that mixtures of these should give both high tensile strength and cool running stocks.

Compound E 1084 (see below), to which the various pigments, both alone and in combination as 30 volumes on 100 parts by weight of GR-S (Buna-S), was used for this and other work described in the remainder of this paper.

Because the cure curve was fairly flat for all pigments, it was not necessary to run a complete range of cures in each pigment or combination of pigments studied to select the best cure for the flexometer tests. A cure of 60 minutes at 292° F was, therefore, used in all cases.

E 1084 Stock

	Parts by weight
GR-S (Buna-S)	100.
Sulfur	2.
Mercaptobenzothiazole	1.5
Zinc oxide*	5.0
Stearic acid	1.0
Bardol	5.0
Pigment*	30 volumes

The results, in this case using Black Label No. 20 zinc oxide of an average particle size of 0.2-micron and easy-processing channel black blends in a 30-volume stock, are shown in Figure 3. These results indicate that one-third of the volume of channel black can be replaced with zinc oxide without appreciably lowering the tensile; while heat generation is greatly lowered. The results show that tensile properties of the blends are greater than would be expected from purely additive properties of the mixtures; while heat generation is lower than would be expected from purely additive properties. The modulus, elongation, and rebound tests are also shown.

The rebound tests were run on a St. Joe inclined-plane rebound tester[2].

Another set of tests was run with a blend of Green Label No. 42, a medium coarse particle-size zinc oxide, 0.28-micron average diameter, and easy-processing channel black. The results (see Figure 4) check those shown in Figure 3 and substantiate the conclusions already shown: namely, that tensile strengths are greater for the blends than would normally be expected for straight mixtures having additive properties, and heat generation is lower for the blends than would normally be expected.

Fine thermatomic-easy-processing channel black.—A similar set of tests was run with blends of fine thermatomic carbon black and channel black in a 30-volume stock (refer to Figure 5). The results indicate tensile strengths of the blends are more nearly additive. Heat generation or heat build-up is lower than would be expected from additive mixtures, but heat generation or build-up is considerably higher than for zinc oxide-easy-processing channel black blends.

Furnace black-easy-processing channel black.—The results of these tests are shown graphically in Figure 6. The tensiles on the mixtures are somewhat

* Five parts zinc oxide present in basic stock E 1084, for activation of 100 per cent carbon black compounds, is in addition to specified volume loadings of zinc oxide, in compounds containing zinc oxide either wholly or in part as pigment loading.

lower than would be normally expected. Since furnace black-easy-processing channel black mixtures are somewhat more difficult to disperse, these results might be expected, however. Heat generation is again higher than for the zinc oxide-easy-processing channel black blends.

COMPARISON OF EASY-PROCESSING CHANNEL BLACK–ZINC OXIDE BLENDS WITH BLENDS OF CHANNEL AND SOFT BLACKS

To compare heat generation and other physical properties of these mixtures, Table I has been prepared, in which the stocks are classified, with heat

TABLE I

COMPARISON OF BLENDS OF EASY-PROCESSING CHANNEL BLACK AND VARIOUS ZINC OXIDES WITH EASY-PROCESSING CHANNEL BLACK-SOFT BLACK COMBINATIONS, CLASSIFIED ACCORDING TO HEAT GENERATION*

Material	Blend† Volumes	Blend† Easy-processing channel black (volumes)	Tensile strength (Lbs./sq. in.)	Elongation (percentage)	Modulus at 400%	Rebound (percentage)
		220° F‡				
Zinc oxide (Green-42)	20	10	1715	530	1050	35.5
Zinc oxide (Black-20)	17	13	2060	557	1220	35.0
Fine thermal black	Minimum temperature with all fine thermal black is 228° F. Tensile strength is 1500 lbs. per sq. in.					
Furnace black	Minimum temperature with all furnace black is 236° F. Tensile strength is 1800 lbs. per sq. in.					
		230° F‡				
Zinc oxide (Green-42)	14.25	15.75	2125	534	1375	34.5
Zinc oxide (Black-20)	13.25	16.75	2410	553	1450	35.0
Fine thermal black	24.5	5.5	1675	543	990	37.3
Furnace black	Minimum temperature with all furnace black is 236° F. Tensile strength is 1800 lbs. per sq. in.					
		240° F‡				
Zinc oxide (Green-42)	9.25	20.75	2425	523	1660	33.75
Zinc oxide (Black-20)	9.70	20.30	2600	562	1630	34.50
Fine thermal black	12.50	17.50	2165	440	1790	34.75
Furnace black	13.75	16.25	2025	383	...	35.5
		250° F‡				
Zinc oxide (Green-42)	4.75	25.25	2570	500	1925	32.5
Zinc oxide (Black-20)	6.00	24.00	2660	515	1875	33.75
Fine thermal black	7.00	23.00	2400	417	2070	33.6
Furnace black	7.25	22.75	2255	418	2200	34.3
		260° F‡				
Zinc oxide (Green-42)	1.5	28.5	2650	478	2125	31.5
Zinc oxide (Black-20)	2.5	27.5	2670	490	2085	32.5
Fine thermal black	2.5	27.5	2575	405	2210	32.7
Furnace black	2.75	27.25	2525	450	2300	33.5
		267° F‡				
Zinc oxide (Green-42)	0	30	2687	450	2231	32.0
Zinc oxide (Black-20)	0	30	2687	450	2231	32.0
Fine thermal black	0	30	2687	450	2231	32.0
Furnace black	0	30	2687	450	2231	32.0

* Data taken from Figures 2 to 6.
† Volumes per 100 parts of GR-S (Buna-S).
‡ Temp. of center of plug at 40 minutes in flexometer.
VL = 485 lbs.
Hd = 0.130 inch.
Two ¼-inch metal-faced plates.

generation as the main criterion. The data were taken from Figures 3, 4, 5, and 6, as shown.

The results are interesting in that to obtain the coolest running stock having reasonable tensile strengths, high zinc oxide-easy-processing channel black blends should be used (see Table II also). Furthermore, for a given

TABLE II

HEAT GENERATION AND TENSILE STRENGTH—ZINC OXIDE AND EASY-PROCESSING CHANNEL BLACK BLENDS

	Zinc oxide no. 20 —10 vols. Easy-processing channel black —20 vols.	Furnace black —10 vols. Easy-processing channel black —20 vols.	Fine therm. black —10 vols. Easy-processing channel black —20 vols.
40 Minutes Temp. (° F)	239	244	244
Tensile strength (Lbs. per sq. in.)	2575	2175	2275
	Zinc oxide no. 20 —15 vols. Easy-processing channel black —15 vols.	Furnace black —15 vols. Easy-processing channel black —15 vols.	Fine therm. black —15 vols. Easy-processing channel black —15 vols.
40 Minutes Temp. (° F)	225	240	238
Tensile strength (Lbs. per sq. in.)	2275	2000	2075

heat generation the zinc oxide-easy-processing channel black blends give higher tensile strengths than the furnace black. On the other hand, for a given tensile strength, the zinc oxide-easy-processing channel black blends give cooler running stocks than blends of easy-processing channel black and furnace black (Table I and Figures 3, 4, and 6).

CONCLUSIONS

A comparative analysis of some of the factors involved in road tests on tires and laboratory flexometer tests indicates that not enough attention has been paid to heat dissipation and the role of the thermal conductivity of stocks in increasing heat dissipation. Flexometer tests currently used, in which samples are flexed between insulated plates, measure mainly heat generation. A modified St. Joe flexometer test is described, using metal-faced plates, which takes into account not only heat generation but heat dissipation, and should more nearly simulate road tests on tires when comparing GR-S (Buna-S) synthetic rubber stocks having different thermal conductivities. Using the new type test, mixtures of easy-processing channel black and zinc oxide are shown to have higher tensile strength and lower heat generation than soft blacks or mixtures of soft blacks and easy-processing channel blacks. The data given in this report indicate the need of further work along this line in the way of road tests on actual GR-S (Buna-S) tires containing zinc oxide in both tread and carcass.

APPENDIX 1

Comparison of Surface Cooling Area Thickness Ratio for Tire in Service and for Laboratory Flexometer Test:

(a) Tire in Service 6.00-16

Outer tire diameter	28 inches
Assume average thickness	0.5-inch
Cross-section circumference of casing from bead to bead	15 inches
Outer radiating area of tire, including tread and sidewall, would be approximately as follows:	$\pi \times 28 \times 15 = 1320$ sq. in.
Ratio of radiating area to thickness of tire in service	$\frac{1320}{0.5} = \frac{2640}{1}$

(b) Regular Laboratory Flexometer Test

Cylindrical plug 1.5-inch diameter, 1.5-inch height

Radiating area $\pi \times 1.5 \times 1.5 = 7.07$ sq. in. lateral surface area of plug

Ratio of radiating area to thickness in laboratory test $\frac{7.07}{1.5} = \frac{4.72}{1}$

It should be noted that radiation on tire is from outer surface only, which is not exactly comparable with laboratory specimen.

(c) Special Laboratory Flexometer Test

Radiating area using two ¼-inch × 3½-inch diameter steel plates is calculated as follows:

Area of surface and side of ¼-inch and 3½-inch diameter steel plate is:

$$\pi \left[(0.25 \times 3.5) + \left(\frac{3.5}{4}\right)^2 \right] = 9.63 + 2.75 = 12.38 \text{ sq. in.}$$

Radiating area of one plate $12.38 - (\pi \times 0.75 \times 0.75) = 10.61$ sq. in.

For two plates, $2 \times 10.61 = 21.22$ sq. in.

Ratio of radiating area to thickness in special test $\frac{21.22 + 7.07}{1.5} = \frac{18.9}{1}$

(Note that ratio of cooling area to thickness in a tire in service is over 560 times that for regular flexometer test

$$\left(\frac{2640}{4.72} = 560\right)$$

and is still 140 times that of special laboratory flexometer test

$$\left(\frac{2640}{18.9} = 140\right)$$

APPENDIX 2

Comparison of Peripheral Speed of Tire in Service and Laboratory Flexometer Test

(a) Tire in Service

Assume 6.00-16 tire on car traveling 35 m.p.h.

R.p.m. around axle $\frac{35 \times 5280}{60 \times 2.3 \times \pi} = 426$

Peripheral speed 35 m.p.h. on outer circumference of tire

Horizontal speed 35 m.p.h., equivalent to 35 m.p.h. wind, neglecting wing drag which will vary with tread design, etc.

(b) Laboratory Flexometer Test

R.p.m. 875

Peripheral speed of outer circumference of test specimen

$\frac{875 \times \pi 1.5 \times 60}{12 \times 5280} = 3.9$ m.p.h.

(Note that peripheral speed of laboratory test-specimen is only one-ninth that of tire in service.)

REFERENCES

[1] "Laboratory tester", Rubber Laboratory, St. Joseph Lead Co., *India Rubber World* **91**, no. 2, 48 (Nov. 1934); A.S.T.M. Standards D623–41T.

[2] In this apparatus, the sample, which may be either a tensile sheet or preferably a specimen ⅜ inch thick, is placed on a sturdy steel inclined-plane (20 inches long, 4½ inches wide, and 1⅛ inches thick) which has been adjusted to an angle of 15 degrees 25 minutes with the horizontal. A ½-inch steel ball held 10½ inches above the sample by a small core electromagnet is allowed to drop on the sample on release of current in electromagnet. The ball bounces off the specimen and lands on the carbon paper on the other end of the inclined-plane at a distance proportional to the rebound of the sample. The ball drops on a piece of carbon paper placed over a sheet of white paper so that the distance is recorded for permanent record by a carbon dot on the white paper. By means of a calibrated chart, drawn from data obtained by dropping a steel ball on a number of samples and measuring the vertical rebound, the percentage rebound is easily obtained.

A DIRECT DETERMINATION OF RUBBER HYDROCARBON. CHROMIC ACID OXIDATION METHOD *

V. L. BURGER, W. E. DONALDSON, AND J. A. BATY

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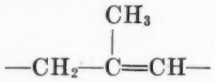
Lack of a practical method for the direct determination of rubber has made it customary to estimate rubber in rubber products by difference[1], a procedure obviously open to large errors of summation and interpretation.

The procedure of Kuhn and L'Orsa[2] for the analytical oxidation of organic compounds using chromic acid was applied by them to numerous compounds, including some containing the structure:



They found that most of the molecule was oxidized to carbon dioxide and water, but that the portion containing a side-chain methyl group formed a molecule of acetic acid, which they separated and estimated. The yield of acetic acid apparently depended on the molecular structure.

A modification of this method was applied to rubber by Kheraskova and Korsunskaya[3]. In a preliminary note they reported obtaining acetic acid from smoked sheet, using steam distillation during the chromic acid oxidation. No details were given. The reported results were 95.3 to 96.5 per cent rubber hydrocarbon content for smoked sheet. These values appear to be based on the generally accepted theory of a polyisoprene structure for rubber hydrocarbon, each isoprene unit having one side-chain methyl group, and the assumption of the formation of one molecule of acetic acid by the oxidation of each isoprene unit.

Of the possible methods for the direct determination of rubber, this was deemed most worthy of further investigation. In this work, the authors have obtained values which indicate a 75 per cent yield in the reaction which forms one molecule of acetic acid from each isoprene unit in rubber hydrocarbon. Because this value was found to be quite duplicable, it was feasible to use the reaction as the basis of an empirical method for the estimation of rubber in rubber stocks.

From the theoretical point of view, this method presents some interesting aspects. The 75 per cent yield of acetic acid was obtained in spite of great variation in the oxidizing conditions, leading to the tentative conclusion that this figure is characteristic of rubber—in other words, that either rubber hydrocarbon is not pure polymerized isoprene or that some of the isoprene units are in a form which does not allow their oxidation to acetic acid.

In spite of the unsatisfactory theoretical basis of the method, it is presented in its present state in the hope that it may be of some value in connection with the present war effort.

* Reprinted from the A.S.T.M. Bulletin, No. 120, pages 23–26, January 1943. This paper was presented at the meeting of A.S.T.M. Committee D-11 on Rubber Products, Atlantic City, New Jersey, June 1942.

The development of chromic acid oxidation as an analytical method for rubber was accomplished in two stages. Investigation was first made to ascertain that the oxidation was quantitative, to establish the type of procedure necessary, and to determine the applicability of the method. When this fundamental work had been done, further investigation was made to simplify the procedure and apparatus.

The determination of rubber by chromic acid oxidation involves four steps: digestion of the sample in the oxidizing mixture, distillation to separate the acetic acid which is formed, aeration of the distillate to remove carbon dioxide, and titration of the acetic acid. The investigation of various phases of the analytical procedure is summarized below.

DIGESTION MIXTURE

Digestion of the sample requires an elevated temperature. Preliminary runs, using a chromic acid-phosphoric acid digestion mixture, indicated that a temperature of approximately 130 to 135 C was necessary for complete digestion of some rubber samples. The volatility of chromic acid under these conditions was sufficient to produce a distillate containing significant amounts of this substance, a situation already encountered by Kuhn and L'Orsa[2].

For convenience in operation, it was desirable to digest at the boiling point of water. To meet this requirement, other mixtures were tried, and it was found that a range of chromic acid-sulfuric acid mixtures was satisfactory. A mixture containing 25 per cent sulfuric acid and 18 per cent chromic acid by weight was found to dissolve crude rubber completely at 100° C within 1 hour. Mixtures containing more than 30 per cent sulfuric acid and 22 per cent chromic acid were found to attack acetic acid in a 2-hour digestion period, as shown in Table I.

TABLE I

OXIDATION OF ACETIC ACID IN 2-HOUR DIGESTION AT 100° C

Composition of digestion mixture (per cent)		Milliequivalents acetic acid taken	Milliequivalents acetic acid recovered	Acetic acid recovered (per cent)
H_2SO_4	CrO_3			
33	24	3.255	3.167	97.3
33	24	3.483	3.302	94.8
31.5	23	3.483	3.455	99.2
30	21.5	3.483	3.476	99.8

The digestion mixture chosen for routine use contains 28 per cent sulfuric acid and 20.5 per cent chromic acid, a more dilute mixture than those which oxidized any appreciable part of the acetic acid. It was found that, in using this digestion mixture under the conditions of the procedure, a distillate containing negligibly small amounts of chromic acid was obtained.

TIME OF DIGESTION

The data on the attack of acetic acid by the digestion mixture (Table I) indicate that a digestion period as long as 2 hours does no harm. Qualitative tests demonstrated that 15 to 30 minutes normally are adequate for digestion, and numerous quantitative tests indicated that the reaction is complete if the sample has gone completely into solution. One-hour digestion time was selected for use in the routine analysis.

RATE OF DISTILLATION

A number of tests were run to find whether it is necessary to control the rate of distillation to obtain satisfactorily reproducible low blank analyses. In all cases, using apparatus as described herewith, and varying the time of distillation from 20 to 90 minutes, the blanks amounted to approximately 0.25 to 0.35 cc. of 0.1 *N* acid per 500 cc. of solution distilled. In like manner it was demonstrated that acetic acid added to the distillation flask was approximately quantitatively contained in the first 300 cc. of distillate, whether the time of distillation was 20 or 90 minutes. Any intermediate rate of distillation is considered satisfactory.

REMOVAL OF CARBON DIOXIDE

It was demonstrated in early experiments that the portion of the rubber hydrocarbon molecule which in the course of the analysis does not form acetic acid is oxidized to carbon dioxide and water. It is necessary to remove any carbon dioxide from the receiving flask before titration of the acetic acid. In testing the present method of removal of carbon dioxide, the authors added carbon dioxide to an aqueous solution containing a known quantity of acetic acid, and passed air through the solution as directed by the procedure. The results indicated that, under these conditions, an aeration period of at least 10 minutes is necessary, but that if the aeration is made at room temperature, a sweeping time as long as 30 minutes does no harm (Table II). An aeration period of 30 minutes was selected for general use in the method.

TABLE II

REMOVAL OF CARBON DIOXIDE FROM DILUTE ACETIC ACID SOLUTION BY AERATION
(Rate of aeration was approximately 2 liters per minute)

Time of aeration (min.)	Volume of solution (ml.)	Milliequivalents acetic acid taken	Milliequivalents acetic acid found	Apparent recovery of acetic acid (per cent)
0	400	3.560	4.730	133
5	400	3.560	3.675	103
10	400	3.560	3.560	100
15	400	3.560	3.554	99.8
20	400	3.560	3.554	99.8
30	400	3.560	3.557	99.9

TITRATION

In following the procedure given in this paper, 30 to 35 cc. of 0.1 *N* sodium hydroxide is normally required. No special technique is involved, since phenolphthalein was selected as the indicator for routine use. The authors consider that in this analysis there may be some advantage in the use of a phenolphthalein-thymol blue mixture consisting of 0.045 gram of phenolphthalein and 0.015 gram of thymol blue dissolved in 30 cc. of 95 per cent alcohol and diluted with 30 cc. of water.

APPARATUS AND REAGENT

Figure 1 gives a diagram of the apparatus. The digestion and distillation apparatus can be conveniently assembled on a ringstand with a tripod foot. The use of rubber connections must be avoided where they might come into contact with the digestion mixture.

The aeration assembly contains a capillary tube which, when connected to the vacuum line, maintains through the receiving flask an air flow of approximately 2 liters per minute. If the pressure in the vacuum line is less than 30 mm. of mercury, an approximately 10 cm.-length of capillary tube of 0.75 mm. bore will maintain the required air flow.

Since it is essential that the aeration be maintained at a rate within 10 to 20 per cent of that specified above, each capillary tube should be tested before

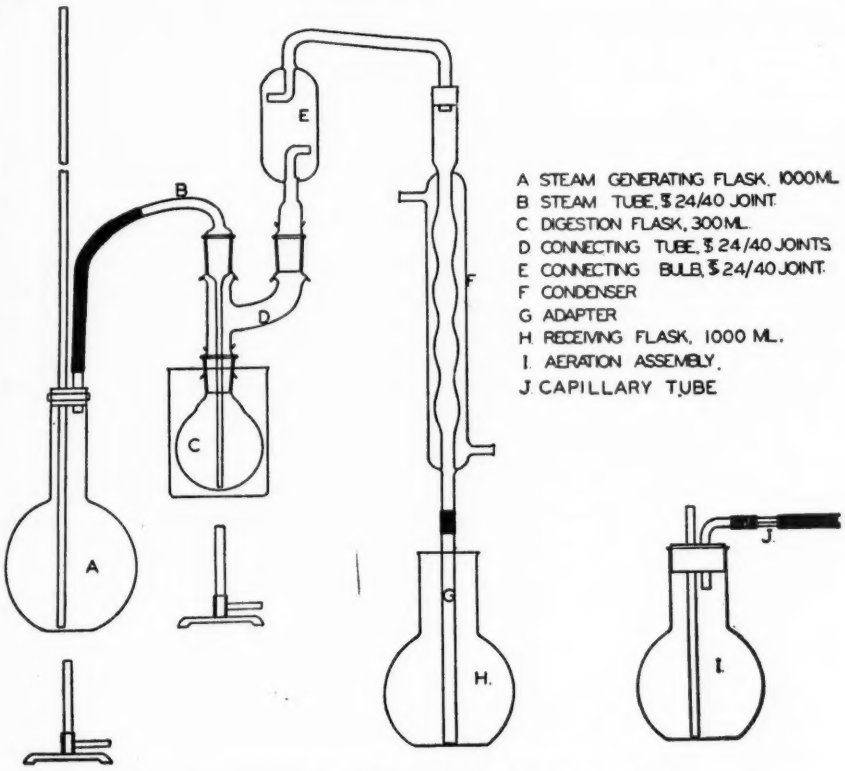


FIG. 1.—Apparatus for direct determination of rubber hydrocarbon.

use. The following method of test is suggested. Invert a graduate over a beaker filled with water and evacuate the air through the capillary by means of a tube extending up into the graduate. The rate of air flow, of course, is the same as the rate at which water fills the graduate.

The chromic acid digestion mixture may be prepared as follows. Dissolve 200 grams of reagent grade chromic oxide (CrO_3) in 500 cc. of distilled water, and add 150 cc. of reagent grade 96 per cent sulfuric acid. Mix well.

PROCEDURE

The procedure consists of the following:

1. Weigh a sheeted sample (0.5 mm. or thinner) of a size sufficient to contain approximately 0.3 gram of rubber hydrocarbon.

Note.—Samples thicker than 0.5 mm. sometimes behave satisfactorily in the analysis. However, thicker sheets of some materials (for example, crude rubber) may not be completely attacked by the oxidation mixture in the time specified for the digestion of the sample.

2. Wrap the sample loosely in filter paper and extract it with acetone for at least 8 hours.

3. In the analysis of vulcanized rubber products, extract with chloroform for 4 hours. In the analysis of crude rubber or poorly vulcanized stocks, omit this step. (Although it is necessary to omit this step when chloroform extraction would remove an appreciable portion of rubber hydrocarbon, the omission, itself, may introduce an error due to the failure to remove certain interferences, if present.)

4. Dry the sample in an oven at approximately 100° C for 1 hour.

5. Set up the apparatus as shown in Figure 1.

6. Place 700 to 900 cc. of distilled water in the steam-generating flask *A*.

7. Place a few cc. of water in the receiving flask *H* (sufficient to cover the end of the adapter).

8. Place 50 ± 1 cc. of digestion mixture in the digestion flask *C*.

[*Note.*—The digestion flask should be marked on the side at a point indicating the liquid level when the flask contains 75 cc.]

9. Lift the steam tube *B*, and insert the sample into the digestion flask *C*. (It is not necessary to quantitatively remove the filter paper from the sample before transferring it to the digestion flask as the interference of small amounts of cellulose is negligible.) Replace the steam tube and tighten the connection.

10. Heat the beaker of water surrounding the digestion flask *C* to boiling. Continue boiling for 1 hour.

11. At the end of this time remove the beaker of hot water from around the digestion flask *C* and remove the burner from beneath it.

12. During the digestion period heat the steam-generating flask *A*, with the stopper removed, until the contents are boiling.

13. Replace the stopper and outlet tube in the mouth of the steam-generating flask and adjust the burner to maximum heat, passing steam through the digestion flask.

14. When the volume of liquid in the digestion flask *C* is increased to approximately 75 cc., place the burner (with a small flame) under it, and keep the flame at a point where it will maintain the liquid at approximately this volume.

15. Continue the distillation until 500 cc. are collected in the receiving flask *H*.

16. Remove the burners, and immediately remove the receiving flask *H* and the adapter *G*.

17. With a wash-bottle rinse the adapter *G*, catching the rinsings in the receiving flask *H*.

18. Adjust the temperature of the liquid in the receiving flask to 25 ± 5 C, insert the aeration assembly into the receiving flask, and attach to a vacuum line. Draw a stream of air through the liquid for 30 minutes at approximately 2 liters per minute. (The rates of loss of carbon dioxide and of acetic acid during aeration have been investigated for the temperature range, type of apparatus and rate of air flow recommended in the procedure. Variation of any of these factors may lead to erroneous analytical results.)

19. Remove the rubber tubing, and loosen the two-hole stopper. With a wash bottle rinse the two-hole stopper and the glass tubing, catching the rinsings in the flask.

20. Add phenolphthalein indicator, and titrate with 0.1000 *N* NaOH (volume *X*).

21. Repeat steps 5 to 8 and 10 to 20 to obtain a blank value for the apparatus (volume *Y*). This should be approximately 0.2 to 0.3 cc.

22. Calculate the results:

$$\text{Percentage of rubber hydrocarbon} = \frac{0.908\ (\text{volume } X - \text{volume } Y)}{\text{weight of sheeted sample}}$$

This calculation is based on the observation that 75 per cent yield results in the reaction:

$$(C_5H_8)_n \xrightarrow{O} nCH_3COOH$$

using purified rubber. To consider the determination on the basis of crude rubber, a suitable correction for nonrubber components is necessary.

APPLICABILITY

The behavior of various rubber compounding materials in the chromic acid oxidation procedure has been investigated, and the findings are summarized in Table III. Though this method of analysis is obviously not specific for natural rubber, none of the common rubber compounding ingredients interferes markedly. No prediction is made regarding possible interference by

TABLE III

DEGREE OF INTERFERENCE OF RUBBER COMPOUNDING INGREDIENTS IN ANALYSIS BY CHROMIC ACID OXIDATION

Material	Interference
Combined sulfur	None in normal soft cures
Carbon black	None as tested in tread stocks
Cellulose	Negligible, equivalent to 2 per cent or less rubber hydrocarbon
Asphaltic hydrocarbon (mineral rubber)	Removed by extraction. If not extracted, equivalent to approximately 45 per cent rubber hydrocarbon
Factice (brown)	Negligible after extraction (in case of samples tested)

TABLE IV

BEHAVIOR OF RUBBERLIKE MATERIALS IN CHROMIC ACID OXIDATION

Material	Value
Hard rubber	Low—approximately 50 per cent of expected value
Balata	Approximately equivalent to rubber
Thiokol-RD	Equivalent to approximately 18 per cent rubber hydrocarbon
Perbunan	Negligibly low—equivalent to 1.5 to 2 per cent rubber hydrocarbon
Buna-S	Very low—equivalent to approximately 3 per cent rubber hydrocarbon
Vistanex	Very low—sample virtually unattacked
Neoprene-GN	Very low—equivalent to approximately 3 per cent rubber hydrocarbon. A modification of the procedure to avoid the interference of chlorine must be used[a]

[a] This modification of the procedure consists in adding neutral potassium iodide to the distillate after aeration (step 19 of the procedure), and titrating any iodine which may be liberated with neutral sodium thiosulfate before proceeding with step 20.

other compounding ingredients, many of which may come into general use in the near future.

In Table IV are listed the results obtained in applying the procedure to some rubberlike materials. The behavior of synthetic rubbers in the analysis is still being studied. Often data obtained by this method of analysis will be distinctly useful in the qualitative analysis of "elastomers" of unknown composition.

TABLE V

REPRESENTATIVE ANALYSES

Sample	Sample weight (g.)	Titration (cc.) (corrected)	Rubber hydrocarbon found (per cent)	Assumed or calculated rubber hydrocarbon content (per cent)
Purified rubber	0.312	34.49	100.4	100
Purified rubber	0.270	30.12	101.0	100
Pale crepe	0.319	33.47	95.3	94 to 95
	0.301	31.15	94.0	
	0.302	31.25	94.0	
	0.312	32.50	94.6	
	0.303	31.68	95.0	
	0.316	32.79	94.2	
	0.303	31.59	94.7	
	0.309	32.26	94.8	
	0.309	32.00	94.0	
	0.3085	32.15	94.6	
	0.320	33.20	94.2	
	0.320	33.22	94.3	
Vulcanizate No. 1	0.438	12.91	26.7	28.2 to 28.4
	0.404	12.35	27.7	
	0.4715	14.95	28.8	
Vulcanizate No. 2	0.3775	22.25	55.1	56.5 to 57.0
	0.367	21.95	55.3	
	0.3605	22.01	55.3	
Vulcanizate No. 3	0.4335	42.15	88.4	89.3 to 90.0
	0.3675	35.93	88.8	
Reclaim I	0.5060	29.20	52.4	56
	0.5130	29.31	51.9	
	0.5000	27.95	50.8	
Reclaim vulcanizate I	0.5005	26.15	47.4	53
	0.5005	26.65	48.3	
	0.5000	26.05	47.3	
Reclaim II	0.5145	33.43	59.0	61
	0.5100	33.79	60.2	
	0.5135	33.40	59.1	
Reclaim vulcanizate II	0.5005	30.55	55.4	58
	0.5005	30.75	55.8	
	0.5000	30.55	55.5	
Reclaim III	0.4995	29.20	53.1	60
	0.5010	28.95	52.4	
	0.5015	28.65	51.9	
Reclaim vulcanizate III	0.5005	26.65	48.3	57
	0.5005	27.05	49.1	
	0.5000	26.65	48.4	
Reclaim IV	0.4990	42.02	76.4	84
	0.4995	42.61	77.6	
	0.5000	42.77	77.6	
Reclaim V	0.5010	30.65	55.6	59
	0.4990	30.59	55.6	
	0.5005	31.03	56.3	

It was found that the method is also applicable to reclaimed rubber, the results being comparable to those obtained with new rubber stocks. Results so far obtained are consistently lower than previously accepted estimates of the rubber hydrocarbon content.

The application of the method to reclaim is being studied further by the Technical Committee of the Executive Committee of the Rubber Reclaimers' Association. The method is now being studied by the Society's Subcommittee XI on Chemical Analysis of Rubber Products, of Committee D-11 on Rubber Products. Some of the details of the present paper are inserted at the suggestion of members of these committees.

ACCURACY

Results may be expected to be accurate within 2 per cent, based on the weight of the sample. Depending on the particular type of rubber, results are usually consistent to 0.5 per cent or less.

In evaluating the accuracy of the method, it should be noted that only in exceptional cases can the true rubber content of a sample be known more accurately than ± 1 per cent.

ANALYTICAL RESULTS

In Table V are listed the results obtained in a number of determinations by the above procedure. These data demonstrate the precision of the method.

SUMMARY

A method for the direct determination of rubber is reported. This method utilizes the property of rubber hydrocarbon when oxidized by chromic acid to form definite and reproducible amounts of acetic acid.

This determination has been reduced to a comparatively simple laboratory procedure, whose accuracy (in the absence of interferences) is 1 to 2 per cent.

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DIGEST OF COÖPERATIVE TEST PROGRAM ON ACCELERATED LIGHT AGING OF RUBBER *

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At a meeting held at the time of the 1941 Spring Committee Meeting, Subcommittee XV on Life Tests for Rubber Products, of Committee D-11 on Rubber Products, decided to conduct a coöperative test to obtain preliminary information with regard to the performance of the Proposed Method of Test for Resistance to Accelerated Light Aging of Rubber Compounds[1].

Although the method as written practically specified the use of the National Carbon Co. 1A Weathering Unit, it was agreed that tests should be made with two other designs of apparatus, and that outdoor exposure tests should be made for purposes of correlation. The three types of apparatus used were as follows:

1. "The Eveready Accelerated Weathering Unit 1A" produced by the National Carbon Co., with a flaming-arc light source at 60 amperes, 50 volts, with radiation filtered through Corex-D glass, samples at a distance of approximately 18 inches from the light source, and subjected to a mild spray of water once every 2 hours.

2. The Weatherometer, Type BWMC, produced by the Atlas Electric Devices Co., using a single neutral carbon arc at 17 amperes and 220 volts, enclosed in a Pyrex glass bowl, with exposed specimens sprayed with water every 20 minutes.

3. The improved Weatherometer, Type DLTS, produced by the Atlas Electric Devices Co., using twin arcs as above, and a cycle of 3 hours' light exposure and 1 hour water spray.

In the course of formulating the test program, it was reported by two laboratories that the rate of deterioration in the tensile strength of rubber exposed in the Eveready equipment with Sunshine carbons and Corex glass filters was no more rapid than in direct summer sunlight outdoors, but that, without the filters, the rate of deterioration was accelerated by a factor of about ten. It was reported also that unstretched specimens deteriorated as rapidly, both on outdoor exposure and in accelerated tests, as stretched specimens, except as affected by cracking, which occurred on stretched samples. Accordingly, both of these facts were considered in the formulation of the program of tests.

Ten laboratories participated in the program, five laboratories using the Eveready equipment, one the Atlas single arc, and one the Atlas twin arc equipment, while five laboratories conducted outdoor exposure tests. However, only four of the latter reported test data. The laboratories participating in the tests were the Atlas Electric Devices Co., Bell Telephone Laboratories, Inc., E. I. du Pont de Nemours and Co., The Firestone Tire and Rubber Co., The B. F. Goodrich Co., The Goodyear Tire and Rubber Co., Manhattan Rubber Manufacturing Division, National Carbon Co., U. S. Navy, Bureau of Ships, and United States Rubber Co.

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The laboratories are designated in the report by letters A to J. The letter designations, however, do not correspond to the above alphabetical listing.

Five typical rubber compounds were selected for testing. These were (1) a tire tread, (2) a white sidewall, (3) a hose cover, (4) a wire insulation, and (5) a Neoprene veneer.

Test sheets, 2 by 6 inches in size, of the compounds were prepared. All cures were considered to be technical. Although the draft as written requires that test-sheets for exposure shall be 0.045 to 0.100 inch think, preliminary experience had shown that, with thinner specimens, deterioration was more rapid. Since it was desirable that results be obtained as rapidly as possible, it was agreed that, for the test program, sheets should be approximately 0.015 inch thick, which was considered to be the practicable lower thickness limit.

The dimensions of the test-sheets, 2 by 6 inches, permitted cutting two tension specimens from each. The A.S.T.M., Type A, 0.5-inch die[2] was used for cutting the tension specimens. The program specified that tension tests should be made not less than 24 nor more than 48 hours after termination of the exposure. It was impossible to adhere to this schedule in many cases.

Four sheet specimens $2 \times 6 \times 0.015$ inches of each compound were furnished to each laboratory for exposure in accordance either with the "Aging Machine" or "Outdoor" schedule as given below.

AGING MACHINE SCHEDULE

Compound 1	Control 100, 150, and 200 hours
Compound 2	Control 25, 50, and 100 hours
Compound 3	Control 100, 150, and 200 hours
Compound 4	Control 50, 100, and 150 hours
Compound 5	Control 100, 150, and 200 hours

OUTDOOR SCHEDULE

Compound 1	Control 50, 100, and 150 days
Compound 2	Control 20, 35, and 50 days
Compound 3	Control 50, 100, and 150 days
Compound 4	Control 25, 50, and 75 days
Compound 5	Control 50, 100, and 150 days

Aging tests, both in machines and outdoors, were started late in May, 1941. The longest scheduled outdoor aging period was completed in late October, 1941.

Specimens were mounted for exposure on tin- or aluminum-covered wood panels. Stainless-steel or monel-metal tacks were used to fasten sheet-specimens to the panels.

The National Carbon equipment was operated without filters, but with the water spray. The Atlas equipment was used with the water spray but not the freezing cycle. Outdoor exposures were at 45 degrees to the horizontal, facing south.

Reports of light intensities for Eveready equipment used by three laboratories, determined by the A.S.T.M. Proposed Method for Calibrating a Light Source Used for Accelerating the Deterioration of Rubber[3], using the decomposition of uranyl oxalate, are given below. Ambient air temperature at the plane of the samples as reported is also given.

Laboratory	Light intensity (mg. of oxalic acid)	Ambient temperature (degrees Fahrenheit)
A	5.6	112
B	...	130
C	5.0	131 to 145
E	6.5	...

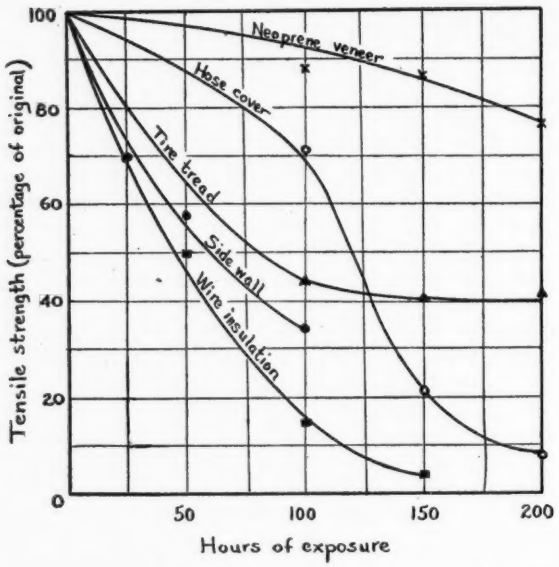

FIG. 1.—Rubber compounds exposed in an Eveready accelerated weathering unit 1-A. Averaged results from Laboratories A, B, C, D and E.

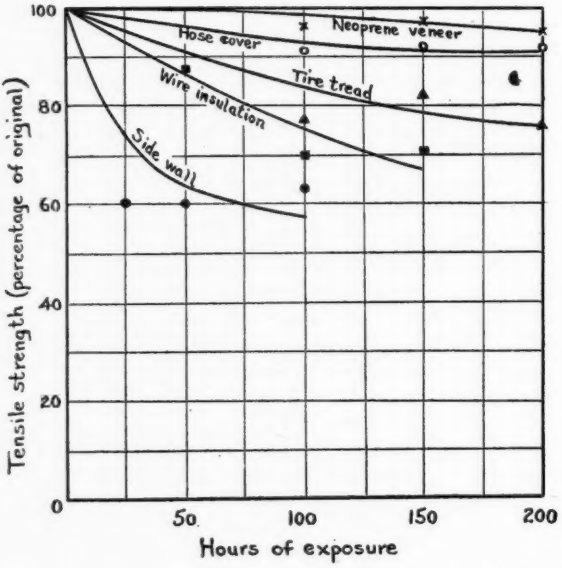

FIG. 2.—Rubber compounds exposed in an Atlas Weatherometer; single arc, Pyrex bowl, water spray. Laboratory A.

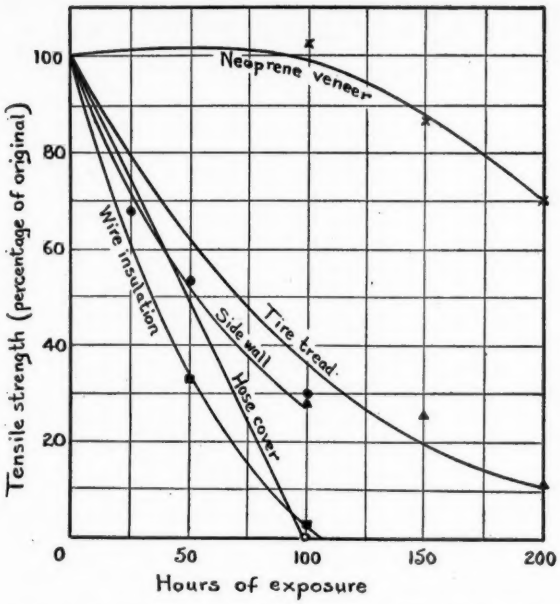

FIG. 3.—Rubber compounds exposed in a New Atlas Weatherometer; twin arc, Pyrex globe, water spray. Laboratory F.

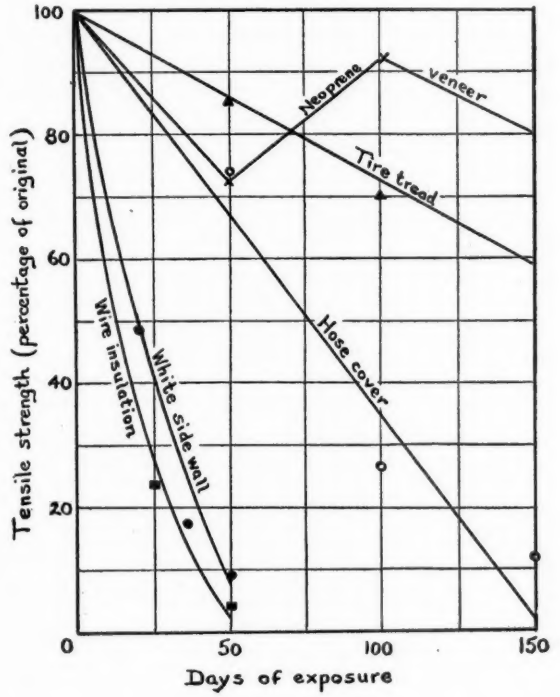

FIG. 4.—Outdoor exposures from May to October 1941. Average of Laboratories A, G and H.

The averaged results of tension tests for each compound from the five laboratories, using Eveready equipment, are plotted in Figure 1. Figures 2 and 3 show the results of tension tests on all five compounds, aged in the Atlas single arc and Atlas twin arc machine, respectively. Figure 4 shows the average of outdoor, direct sunlight aging for the five compounds.

DISCUSSION

The final tensile strength results, both in the light aging machines and in direct sunlight, show the Neoprene veneer stock to be most resistant to deterioration. In all cases the same order of evaluation was obtained in the Eveready equipment as in outdoor aging. The order of evaluation by the various test methods follows:

Outdoor	Eveready	Twin arc	Single arc
Neoprene	Neoprene	Neoprene	Neoprene
Tire tread	Tire tread	Tire tread	Hose cover
Hose cover	Hose	Sidewall	Tire tread
Sidewall	Sidewall	Hose cover	Sidewall
Insulation	Insulation	Insulation	Insulation

Among the various laboratories using the Eveready equipment, Laboratory A was most severe with each of the five compounds. In the case of the tire tread compound, Laboratory A showed a final deterioration of about 80 per cent. Deterioration with the same equipment in the other four laboratories varied from about 50 to 63 per cent. In the case of the white sidewall compound, Laboratory A showed a deterioration of over 90 per cent, Laboratory B almost 80 per cent, and the other three laboratories between 50 and 60 per cent. In the case of the hose cover compounds, Laboratories B, D, and E reported results reasonably close together with Laboratory A results most severe and Laboratory C reported intermediate results which were less severe but quite well in line finally. All results in the case of the wire insulation compound showed deteriorations over 90 per cent. Variations of 15 to 37 per cent deterioration were reported from the five laboratories for the Neoprene veneer compound.

Among the four laboratories reporting outdoor exposure tests, the variations in final deterioration for the white sidewall and insulation compound were quite consistent. In the case of the other three compounds, the results of three laboratories were consistent, Laboratory A being more severe in the case of the hose cover and Laboratory J being more severe with the tire tread and Neoprene stock.

A possible cause for variations in results reported for Eveready exposure is variation in temperature. Only three laboratories reported ambient temperatures adjacent to exposed specimens. These varied from 112° to 145° F, the latter being reported by Laboratory C. Variations in outdoor aging results may be accounted for by variations in locality, local temperature, prevalence of dust, rainfall and other climatic conditions.

The single-arc Weatherometer showed little deterioration compared with the other exposures. The twin-arc Weatherometer gave results which were somewhat more severe than the average of those obtained by the five laboratories which used the Eveready equipment.

The degree of deterioration obtained in the Atlas twin-arc Weatherometer and the average for the Eveready compared with the average deterioration obtained on outdoor exposure varied considerably for the five compounds

tested. The approximate times of exposure in the machines in hours equivalent to 1-day outdoor exposure are given below.

Compound	Eveready	Atlas twin-arc
Tire tread	1.5	1.0
White sidewall	2.7	2.5
Hose cover	1.4	0.6
Insulation	3.0	1.9
Neoprene	2.5	1.9
Average	2.2	1.6

Visual examination of weathered specimens demonstrated clearly differences in character of the weathered surface layers, not only between the naturally and artificially weathered samples but, to a lesser degree, between the weathering units of the different laboratories. This indicates a lack of uniformity in performance of the weathering units, which may result from differences (1) in location, which lead to differences in temperature, (2) in the character and volume of the water supply, (3) in the cycle, (4) in the position of the sample in the unit, which affects the way in which the sample is hit by the water spray and the volume of water passing over its surface, (5) in the manner of support, and so on.

Removal of the filters unfortunately results in a disturbance of the ventilation conditions around the arc and an increase in the temperature at the sample. Considerable heat aging must have occurred, which is not differentiated from the light aging. That the temperature of exposure was too high is indicated by the fact that some of the samples—particularly Compound 3—became tacky on the side remote from the light source.

Although the appearance of the surfaces was of the same general character in the specimens weathered in the Eveready unit, it was definitely different from that of the outdoor specimens. In the case of Compounds 1 and 3, for example, the surface skin tended to bend down into the cracks in the outdoor samples, while the Eveready unit samples produced patches of skin, with a tendency to curled-up edges giving the appearance of flaking. The Weatherometer samples had, in general, skins of finer texture than the others.

From these observations it would appear that a problem to be solved is to secure uniformity in performance between identical units operated in different laboratories. To this end it would seem advisable to make a much more detailed study of a single compound to establish the reasons for departure from such uniformity.

CONCLUSION

The Eveready unit without filters and the Atlas Twin-arc Weatherometer effect a more rapid deterioration of vulcanized rubber on exposure than does ourdoor exposure in summer. The degree of acceleration varies with the particular compound tested. In these tests it was found that from 0.6 to 3.0 hours' exposure in the machines, depending on the compound, was equivalent to 1 day of outdoor summer exposure. The procedure followed in making Eveready tests is not sufficiently standardized to obtain satisfactorily comparable results in several laboratories, with a wide variety of compounds. The Atlas single-arc equipment shows little acceleration in aging rate compared with the Atlas twin-arc and Eveready equipment used in these tests. No broad conclusions can be drawn from the results of tests in the Atlas twin-arc

equipment, since results were reported for only one of these machines. It is suggested that measurements of the total radiation may be of greater significance than measurements in the ultraviolet region alone. Further standardization in connection with ventilation and maintenance of a constant uniform temperature around the exposed specimens appears desirable. Further work is required to determine the effect of the thickness of the exposed sample on the rate of deterioration. If exposure periods are to be for time periods such as were used in these tests, it may be desirable to use thicker specimens.

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DETERMINATION OF TOTAL SULFUR IN RUBBER AND RUBBERLIKE MATERIALS *

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The determination of total or combined sulfur in vulcanized rubber and materials of similar type involves numerous difficulties. This fact is attested by the very large number of methods which have been proposed[1].

All the most important methods involve oxidation of the sulfur, in whatever form it may be present, to sulfate and weighing the latter as barium sulfate. The only essential differences lie in the methods of oxidation employed.

The methods which seem to be the most popular at the present time are (1) oxidation of the sample in a Parr bomb with sodium peroxide, potassium chlorate, and sugar[2]; (2) oxidation with perchloric acid and nitric acid[3], sometimes with the additional use of bromine[4]; (3) oxidation with nitric acid and bromine, followed by sodium carbonate-potassium nitrate fusion[5]; and (4) oxidation with nitric acid-zinc oxide mixture, bromine, and potassium chlorate[6].

Serious explosions have been known to occur with perchloric acid oxidations; hence this method is not so popular at present as the other three. The fusion methods are reliable, but they are time-consuming and therefore not convenient when large numbers of samples must be handled.

Methods (3) and (4) have been for a number of years the preferred procedures of the A. S. T. M. For several years the fusion method was the "recommended" one and method (4), commonly referred to as the "Kratz-Flower" method, was listed as the "alternate" method[7]. In 1940 the order of listing was reversed[8], so that the Kratz-Flower method became the recommended and, at least inferentially, the preferred procedure.

This procedure involves preliminary oxidation with nitric acid and bromine, following which the mixture is slowly evaporated to a foamy sirup. Then, if organic matter or carbon remains at this point, a few milliliters of fuming nitric acid and a few crystals of potassium chlorate are added, and the solution is evaporated at a boil. The operation is repeated until all carbon is gone and the solution is clear, colorless, or light yellow. It is then evaporated, and nitrates are decomposed by one of two alternate methods.

The analyst is cautioned to use care during the addition of potassium chlorate. This is a standard precaution, to be found in all analytical textbooks. That it is well founded is proved by the fact that explosions frequently occur when the addition is carried out in this manner.

An additional disadvantage of this standard procedure is the fact that the seemingly drastic conditions of oxidation are still not sufficient to effect the oxidation of many samples. Carbon black is oxidized in some samples, but not in others. Some of the synthetic rubbers prove especially troublesome, as the solution reaches a dark, nearly black color, which is not destroyed by repeated treatment.

A somewhat unorthodox modification of the above procedure has been found to take care of these difficulties and to yield a clear, light-colored solu-

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tion, with considerably less trouble. The writer does not claim to have originated the method; in its present form it is an adaptation of a general procedure with which he came in contact a number of years ago and the exact origin of which is not known. Meantime, the method has been extensively tested, in the hands of both experienced analysts and students who were completely unfamiliar with the procedure. A number of variables affecting the procedure have thus been studied in some detail, and the operating details as indicated here are believed to be general in their application.

MODIFIED METHOD

In the standard method as modified, the nitric acid-bromine oxidation is carried out as usual. Then the resulting solution is evaporated slowly until no more nitrogen oxide or bromine fumes are visible, diluted with 10 to 15 ml. of concentrated nitric acid, and heated to boiling. To the vigorously boiling solution are added successively several 0.5-gram portions of potassium chlorate.

Contrary to what one might expect, no explosion occurs. This procedure has been employed in hundreds of analyses of various types of rubber products, and explosions have occurred only where the solution was allowed to cool and was no longer boiling vigorously.

Carbon black is oxidized readily by this method, and the dark-colored solutions obtained from vulcanized synthetic rubber samples are readily decolorized to yield usually straw-colored solutions. If the successive portions of chlorate are added too rapidly, foaming may result. An occasional sample foams when companion samples do not; this variance may be due to the presence of certain compounding ingredients. A little practice will enable the analyst to anticipate cases of bad foaming, and to control them by quickly removing from the heat during the early stages of foaming, and, if necessary, cooling under tap water.

The exact amount of chlorate necessary to effect the oxidation varies with the individual sample. This is particularly true of those containing carbon black. The relative ease of oxidation seems to be related to the type of black. In general, any unnecessary excess of chlorate should be avoided, to prevent contamination of the barium sulfate precipitate by other salts. A large excess of chlorate definitely tends to favor coprecipitation.

Since potassium chlorate is somewhat difficult to obtain in war time, a number of determinations have been made with an analytical grade of sodium chlorate. The sodium salt may be substituted for the potassium with no noticeable loss in efficiency, but where both are available, the potassium salt is preferred, as it can usually be obtained in a higher state of purity.

Following the chlorate treatment the normal procedure may be employed, with no additional modifications.

This general method for the determination of sulfur is also adapted for the analysis of various sulfur-containing compounds, especially organic ones. It is reasonably convenient and merits more attention than it has received in the past from those engaged in analyzing materials other than rubber. It has been used successfully by the writer in analyzing a wide variety of sulfur compounds; none of those investigated have failed to be oxidized by this method. However, it is not a completely universal method, and some judgment must be exercised in its use. In the case of long-chain organic sulfur compounds of very considerable molecular weight and relatively high sulfur content[9], the recurrence of units in the chain of the type—RSR—is common

and on oxidation can give rise to sulfones of such stability that even the sodium peroxide fusion method very frequently leads to low results. The only method that gives consistently accurate results in the case of this type of compound involves the practically instantaneous oxidation of the sample in a bomb under about 30 atmospheres of oxygen pressure.

Many organic compounds are completely oxidized by the nitric acid-bromine combinations, and the chlorate is then unnecessary.

In Table I are listed a few of the more typical results obtained by this procedure. The Parr bomb fusion with sodium peroxide was chosen as a

TABLE I

TYPICAL SULFUR DETERMINATIONS

Sample	Theoretical	Parr bomb	Modified A. S. T. M.
Rubber stock A	...	2.42	2.50
		2.45	2.45
Rubber stock B	...	1.80	1.80
		1.85	1.84
Rubber stock C	...	3.05	3.10
		3.09	3.14
Hycar-OR stock	...	2.76	2.80
		2.80	2.81
Buna-S stock A	...	1.76	1.78
		1.80	1.78
Buna-S stock B	...	1.42	1.37
		1.40	1.42
Thiokol stock	...	47.20	47.30
		47.38	47.42
Mercaptobenzothiazole	38.42	38.28	38.50
		38.42	38.40
Ethyl-*p*-toluenesulfonate	15.98	16.00	16.00
		15.98	15.95
Thiocarbanilide	14.04	14.17	14.10
		14.12	14.17
n-Butyl sulfite	16.48	16.32	16.40
		16.37	16.47

reference method for these samples. The agreement between these two methods is good, and the analytical results for the pure compounds check well with the calculated values.

COMPLETE PROCEDURE

Place 0.5 gram of soft rubber or 0.2 gram of hard rubber in a 500-ml. Erlenmeyer flask of chemically resistant material (Pyrex, quartz, etc.), add 10 ml. of zinc oxide-nitric acid solution (containing 200 grams of zinc oxide to 1000 ml. of nitric acid, specific gravity 1.42), and moisten the sample thoroughly. Let stand at least 1 hour, overnight if convenient. The sample becomes partly decomposed; this permits the addition of fuming nitric acid with no danger of ignition of the sample. Add 15 ml. of fuming nitric acid and whirl the flask rapidly to keep the sample immersed to avoid ignition. With some samples it may be necessary to cool the flask under running water.

When the solution of the rubber appears to be complete, add 5 ml. of a saturated water solution of bromine and slowly evaporate the mixture until no more fumes of nitrogen oxide or bromine are visible. Dilute the solution with 10 to 15 ml. of concentrated nitric acid and heat to boiling. To the vigorously boiling solution add about 0.5 gram of potassium chlorate (or an

analytical grade of sodium chlorate). If the solution is still dark, continue to boil and add another portion of chlorate. Continue the addition of successive portions of chlorate until all carbon is gone and the solution is clear, colorless, or light yellow. Do not use an excess of chlorate over the amount required to complete the oxidation. (Caution: Foaming may result if the portions of chlorate employed are too large or if the successive portions are added too rapidly.) If foaming starts, cool immediately, if necessary under running water.

Evaporate the mixture to dryness and bake at the highest temperature of a Tirrill burner until all nitrates are decomposed and no more nitrogen oxide fumes can be detected. Anneal the flask carefully to prevent cracking.

Add 50 ml. of hydrochloric acid (1 to 6) to the cooled flask and digest warm until solution is as complete as possible. Filter the solution, wash the filter, and dilute the solution to 300 ml. Add 10 ml. of saturated picric acid solution, precipitate with 10 per cent barium chloride, and allow the precipitate to stand overnight. Filter, wash with hot water until the filter paper is colorless, and determine the barium sulfate precipitate in the usual manner.

ACKNOWLEDGMENT

A considerable number of people have contributed to this study over a period of several years. The author is grateful to all of these and especially to Robert W. Duncan and Arthur L. Robinson, who carried out a number of the determinations with the synthetic rubber samples.

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EVALUATION OF SMALL AMOUNTS OF SYNTHETIC RUBBER *

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In research on rubber synthesis, as in any broad program of chemical research, it is a distinct advantage to be able to do all work on a normal laboratory or test-tube scale. With rubber, however, the standard laboratory testing methods require from 200 to 500 grams of rubber for each batch. Hence it was obvious that, if the advantages of small-scale work in the preparational stages were to be realized, a new technique of rubber testing would have to be developed.

The use of entirely new and unrelated procedures has two definite objections. In the first place the new procedures must be thoroughly tested and compared with the older methods of testing or with the processing and use requirements of the new rubbers. In the second place the significance of the results of such new tests can be conveyed, even to experienced rubber technologists, only after considerable interpretation of the methods. It seemed best, therefore, to modify standard rubber-testing methods so that they could be applied to very small amounts of synthetic rubber.

More recently, the shortage of natural rubber has made necessary a reduction in the amount of rubber used for testing. For this purpose the same small-scale procedures are highly advantageous.

While some idea of the quality of a sample of natural or synthetic rubber can be obtained from examination of the crude rubber itself, it is much better to know the physical properties of the vulcanized product. This means that one or more balanced compounds must be mixed and tested.

The purpose of this paper is to describe a technique which has been developed in the Goodrich laboratories whereby, with as little as 5 grams of rubber, the stress-strain characteristics may be determined, and with 9 grams of rubber a fairly comprehensive evaluation can be made. This method has been used to evaluate polymers made on the 10-gram scale by Fryling[1].

COMPOUNDING AND MIXING

For weighing some of the ingredients of a 10-gram batch (in this paper the batch size is given as the number of grams of crude rubber in the batch), it is necessary to use an analytical balance and make weighings to the closest milligram. For other weighings a triple-beam balance accurate to 0.1 gram is satisfactory. The guide is the accuracy required to avoid significant changes in the recipe due to errors in weighing. Tarry softeners may be dissolved in a solvent and measured volumetrically, allowing the solvent to evaporate before use. Pigments may be kept in cellophane envelopes. Softeners, sulfur, accelerators, etc., may be kept in small aluminum dishes or in bottle caps (see Figure 1).

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These small batches are mixed on special mills with rolls 4 inches in diameter. The first mill used was made in the Goodrich shops and is shown in Figure 2; the distance between the guides is 2.5 inches. The second mill was

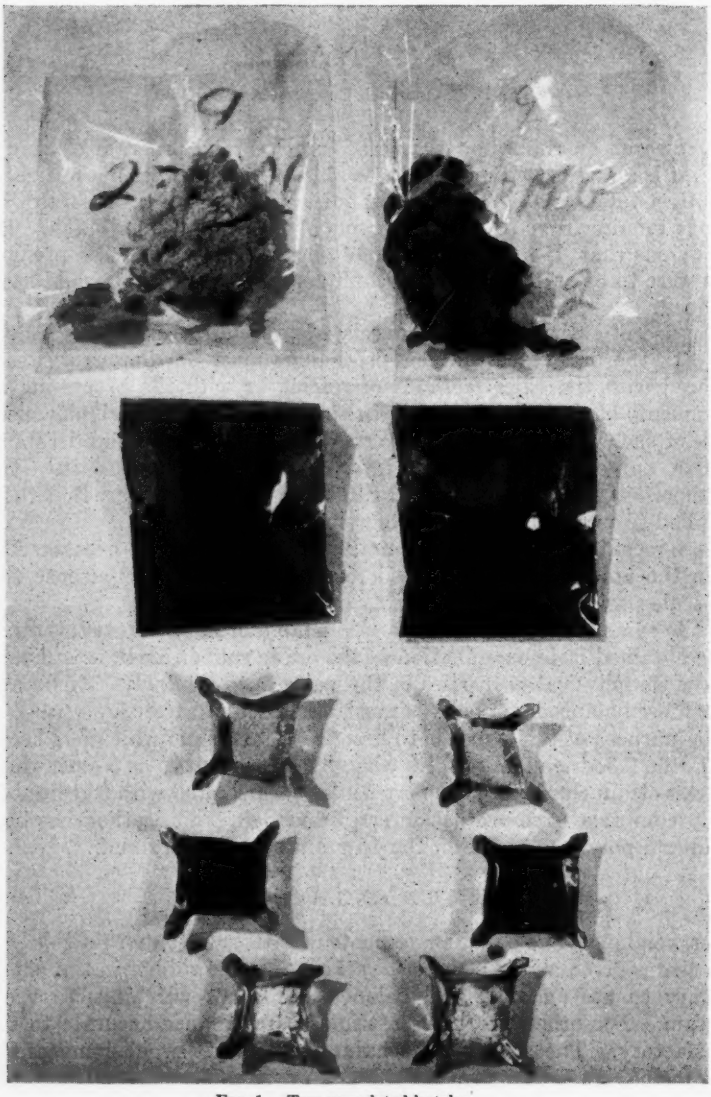

FIG. 1.—Two completed batches.

made by the National Rubber Machinery Company (Figure 3), and the distance between the guides can be varied from 1 to 4 inches. Both mills are connected with steam and cold water. The gear ratios for the rolls are 1.47. The speed of the slow roll is 10.5 r.p.m., or a surface speed of 11 feet per minute.

The milling procedure and mill temperature depend on the type of rubber being tested.

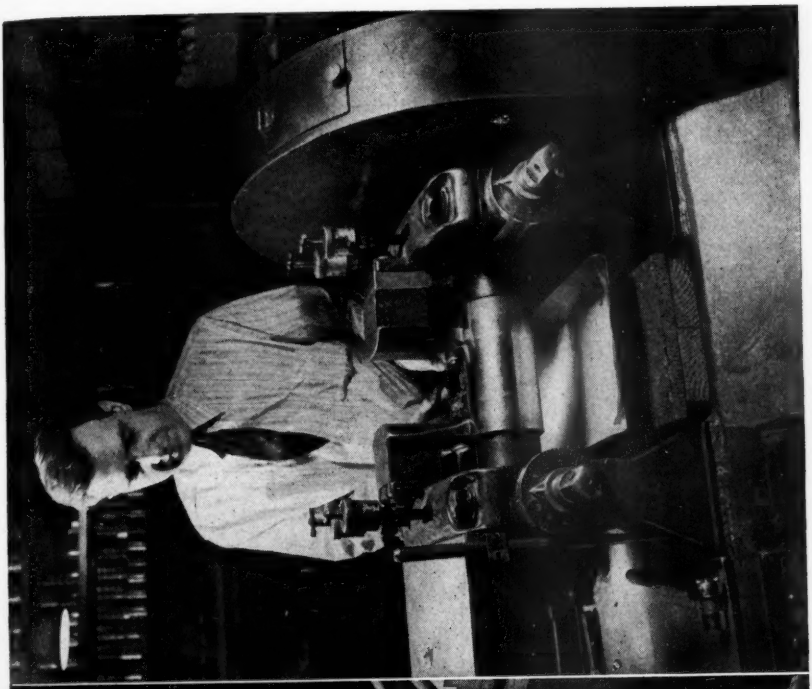

FIG. 3.—National machinery company mill.

FIG. 2.—Goodrich mill.

EVALUATION OF PROCESSING PROPERTIES

Processing properties are evaluated on both the crude synthetic rubber and on the mixed batch. For the crude material the ease with which a smooth band is formed on the roll, the extent of the breakdown, and the time required for breakdown are significant. In addition, the ease of adding the various components, the degree of dispersion, and the total batch time are significant for the mixed batch.

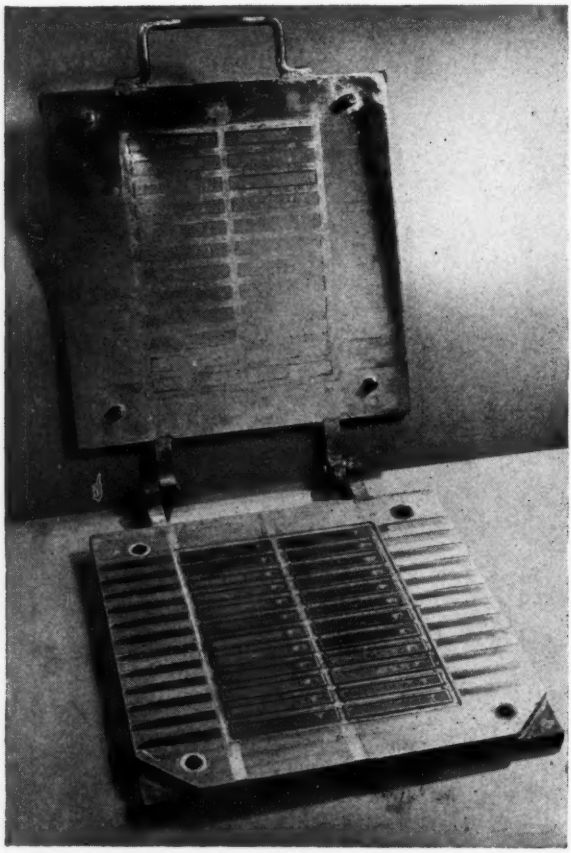

FIG. 4.—Mold for curing specimens.

Milling behavior.—The general appearance and feeling of the stock on the mill are good indications of its milling behavior. A good stock gives a smooth shiny band on the mill roll, and can be pulled easily into long strings. Other batches may break short when pulled out. They may be ragged and cracked at the edge of band. They may be dull or rough in appearance. They may crack across the whole band and become lacy. In extreme cases the stock falls off the rolls.

The thickness of the band on the roll may be important. Some stocks mill well on a tight mill, but become cracked and lacy on a loose mill. The

batch is usually mixed with a rolling bank and, to evaluate milling behavior, the appearance is noted at this stage and also with the rolls opened until the bank almost disappears.

Temperature is likewise an important consideration in processing. Factory batches are normally mixed with stock temperatures between 140° and 260° F. On the small mills with the cold water on, the stock temperatures may be between 60° and 100° F. It is essential to know how a stock behaves at different temperatures. With small batches on the small mills, the stock temperature can be controlled within a range of about 5° F by running steam or water through the mill rolls. The temperature is measured by a special needle pyrometer, assembled by P. R. Tarr of the Goodrich Physics Research

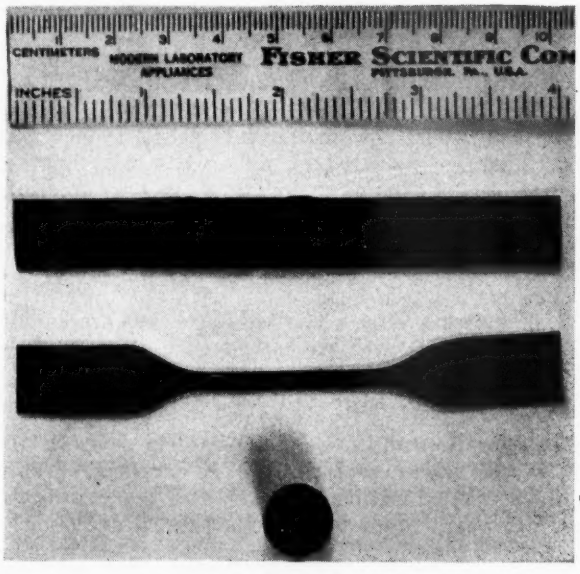

FIG. 5.—Test specimens.

Laboratory. By observing the milling behavior at different stock temperatures, it is possible to make a fairly accurate prediction as to the way a stock will behave in factory operations.

Plasticity.—With such small batches standard specimens for determining plasticity cannot be obtained. It has been found, however, that moulded hardness pellets can be used, for comparative purposes, in the Goodrich plastometer. If the sulfur is omitted from the batch and the pellet moulded 30 minutes at 250° F, the plasticities are reasonably close to those of the milled batch.

Tackiness.—There seems to be no quantitative measure of building tackiness, and its evaluation is one of feeling and experience. It is estimated merely by sticking pieces of the rubber together, on and off the mill, and pulling them.

General comments.—It is obvious that much of this evaluation of processing characteristics is neither objective nor quantitative, but depends to a large measure on the skill and experience of the operators. Its successful use in this laboratory has been due in large measure to the conscientious care and obser-

vation of D. E. Henderson, D. V. Sarbach, D. E. Sauser, W. B. Fox, R. W. Ihnot, and R. F. Coate. Also in this type of work it is important that all concerned "speak the same language". Many important details are almost impossible to describe accurately. Close coöperation is necessary, and frequently the whole group must watch a batch together and agree to use certain words to describe what they see at definite stages.

VULCANIZATION OF TEST-SPECIMENS

Stress-strain.—For stress-strain measurements, the test specimens are strips 4 inches long, 0.5 inch wide, and 0.025 inch thick. These are cured in a polished, chromium-plated mold (Figure 4). The identifying markers are of 0.001-inch aluminum sheet, with the lettering made in a typewriter without the ribbon. The batch stock is sheeted off the mill at the desired thickness and pressed under a flat weight for about half an hour before the strips are cut. Strips are always cut with the grain of the stock.

Hardness, rebound, compression-set.—These three measurements are made on the same specimen, which is a small disk or pellet, ½ inch in diameter and ⅜ inch thick. They are prepared by rolling the stock on the mill to the necessary diameter and cutting off cylinders, which are cured in a three-plate mould. The test-specimens are shown in Figure 5.

Rapid flex hysteresis.—For these tests special cylinders are moulded in the same manner as the hardness pellets. The cylinders are 0.7 inch in diameter and 1 inch thick.

Time and temperature of cure.—The test-specimens are cured at any time and temperature compatible with the compound used.

TESTING VULCANIZED SPECIMENS

Stress-strain.—For use with the small tensile strips, a special dumbbell with a ⅛-inch narrow section was designed by Z. E. Sargisson[2]. These specimens are cut from the strips with a die. In each case the strip is cut on a fresh surface of hard cardboard to ensure the smoothest possible cut. The stress-strain measurements are made on a Scott tensile tester for thin sheets, with the weight adjusted for the narrow dumbbell.

Hardness.—Durometer hardness is measured on the hardness pellet.

Rebound.—For measuring rebound, a metal block, ⅜ inch thick, with a suitable hold in the middle, is placed in a Schopper rebound machine. The hardness pellet is placed in the hole and the rebound determined by the Schopper pendulum hammer method[3].

Compression-set.—The hardness pellet is also used to measure compression-set. This can be done either at constant load or at constant deflection. For general testing, constant deflection method is decidedly preferable because a number of specimens can be put in one jig, and this jig is simpler than that required for constant load. Except for the size of the specimen, the regular A. S. T. M. procedure[4] is used, *e.g.*, 40 per cent compression for 22 hours at 158° F.

Immersion tests.—The special procedure for immersion testing has already been described[5]. Briefly, it consists of placing a narrow die-cut strip in a small glass tube and measuring the increase in length through the glass tube after the specified immersion. The corresponding volume increase is read from a prepared table. Five immersion specimens can be cut from one tensile strip.

Although the change in length is measured in only one direction, the results seem to be sufficiently accurate for preliminary evaluation of a synthetic rubber.

Freezing tests.—The broken ends of the dumbbells, trimmed to 1 × 0.5 inch, are used for determining freezing temperatures. Four measurements are made as the temperature of a methanol bath is lowered in increments of 5°, starting at 7.5° C. At each temperature the specimen is either good or bad. The temperature halfway between the last good (+) temperature and the first bad (−) temperature is reported as the freezing temperature with respect to that test.

A is the test for freezing with respect to spontaneous recovery. The specimen is bent double in a clamp. The clamp is suddenly opened and, if the specimen opens up so that it does not fall out, it is good. If it remains folded and falls out, it is bad.

B is flexibility under a dead weight of 50 grams. A rod of this weight is rested on the end of the specimen, which is held horizontally in a rack. If the sample bends it is flexible.

C is the flexibility under a load of 250 grams. The procedure is the same as for *B*.

D is the brittle temperature. The rod is rested on the end of the specimen, which is hard enough to hold it without bending, since it is not flexible in the *C* test. The top of the rod is then tapped with a hammer. If the specimen cracks it is brittle.

Rapid flex hysteresis.—The special pellet has the dimensions of the standard specimen used in the Goodrich flexometer[6]. The test is run by the standard procedure.

Complete evaluation of 9 grams of rubber.—With 9 grams of rubber, using a tread-type recipe, the batch is mixed. Breakdown, ease and time of mixing, tackiness, and behavior on the mill at 100°, 160°, and 180° F are noted. One strip is cured 20 minutes, two strips are cured 30 minutes, and three strips are cured 45 minutes, assuming an optimum cure at 30 minutes and slight overcure at 45 minutes. Hardness pellets are cured 30 and 45 minutes.

Stress-strain measurements are made on all strips except one of those cured 45 minutes. Hardness, rebound, and compression-set are measured on each pellet. The extra strip is used to determine swelling in hexane, benzene, acetone, and alcohol at room temperature and in Circo light-process oil at 180° F. Freezing characteristics are determined on the ends of the broken dumbbells for the 30- and 45-minute cures.

With this information, it is possible to tell whether or not the product is worth further development. In fact it is possible to make a fairly good estimate of its commercial possibilities.

ADVANTAGES AND DISADVANTAGES OF THE PROCEDURE

Disadvantages.—The most obvious disadvantage of this procedure is the repeated use of single test-specimens. With a single specimen there is no chance to check results, and accidental defects may spoil the test. The use of the same specimen for measuring hardness, rebound, and compression-set may alter the results somewhat. Another objection is the probable presence of calender grain in the tensile strips. Probably the greatest objection, particularly in its application to natural rubber, is the excessive breakdown obtained in the milling of small batches. Because synthetic rubbers do not break down to the extent that natural rubber does, this has not been a serious problem,

provided it was recognized. With natural rubber it is necessary to use a warm mill and mix the batch rapidly. It has been possible to adopt the small mill procedure to the use of natural rubber batches containing somewhere between 10 and 50 grams of rubber.

Advantages.—The outstanding advantages of this procedure are the small amounts of material required and the speed with which the work can be done. Another advantage is the accurate control of mill and batch temperatures. This makes possible the observation of milling behavior at specified temperatures, which is useful in predicting factory processing characteristics. A number of comparisons have shown that conclusions based on experiments on the 4-inch mills agree well with those based on experiments run on the standard 12-inch experimental mills. Although the rapid adoption of a new material into factory production depends primarily on the skill of the factory operators, considerable confidence in this 10-gram procedure has been gained from the fact that, on more than one occasion, it has been possible to go from 10-gram operations to factory production in a very short time. The predictions made from small-scale evaluations have been in large measure fulfilled in production.

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IDENTIFICATION OF CARBON BLACK BY SURFACE-AREA MEASUREMENTS *

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Parkinson[1] has suggested that the particle size of lampblack recovered from a tire-tread stock by means of nitric acid is unchanged from that of the original supply. His conclusions were drawn from sedimentation experiments. The authors have found[2] that the low-temperature nitrogen-adsorption method of Emmett and his coworkers[3] for determining surface areas of finely divided substances is a comparatively rapid and accurate method of measuring the total surface of commercial carbon blacks. The object of the present investigation was to expand Parkinson's observation to a variety of commercial carbon blacks, employing the nitrogen-adsorption technique. Since the surface-area of most of the standard carbon blacks has been previously determined[4], a method of identifying the carbon black present in an unknown rubber stock can be readily devised if it is first established that carbon black can be recovered from a rubber stock with unchanged surface-area.

The present paper reports the surface-area values determined by the nitrogen-adsorption method of a number of commercial carbon blacks recovered from vulcanized tread stocks.

EXPERIMENTAL DETAILS

The technique and apparatus for determining the surface-area of carbon black by the low-temperature nitrogen-adsorption isotherm have been described in a previous publication[2]. An oxygen thermometer is now used to measure the temperature of the liquid nitrogen bath during a run. From this temperature, the appropriate saturation pressure, p_0, of the adsorbate nitrogen is obtained and employed in calculating the final surface-area value[5].

The carbon blacks studied were compounded in the following recipe:

Ingredient	Parts by weight	Ingredient	Parts by weight
Smoked sheet	100	Mercaptobenzothiazole	0.9
Zinc oxide	5	Stearic acid	4.0
Sulfur	3	Agerite-Hypar	1.0
Pine tar	3	Black	45

One stock was made from Grade-6 carbon black in Buna-S:

Buna-S	100
Zinc oxide	5
Sulfur	2
Pine tar	2
B-L-E (antioxidant)	1.0
B-J-F (accelerator)	1.5
Laurex	2
Grade-6 black	50

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The smoked sheet stocks were cured for 30, 60, and 90 minutes at 134° C; the Buna-S stock at 144° C. The 60-minute cure was nearly optimum in the majority of cases, and was the only cure selected for study.

The following commercial carbon blacks were selected for study:

Gastex, a nonimpingement-type black manufactured from natural gas. A semireinforcing black of the "soft" type widely used in rubber goods.

Acetylene black (Shawinigan), prepared by thermal decomposition of acetylene. A soft-type black which does not possess the marked rubber-reënforcing properties of channel blacks. Its electrical conductance in rubber stocks is very high.

Spheron, grades 9 through 1, a series of rubber-reinforcing carbon blacks prepared by impinging natural gas flames on metal surfaces. Their essential difference is particle size, grade 9 being the coarsest and grade 1 the finest of these typical rubber blacks.

Spheron N, a channel black of fine particle size with superior electrical conducting properties when compounded in rubber stocks.

The free carbon in the vulcanized rubber stocks was separated by means of nitric acid. The procedure followed was essentially that of Oldham and Harrison[6].

In the authors' laboratory it is the practice to employ a 0.75- to 1.00-gram sample of rubber stock instead of the 0.15-gram sample suggested by Oldham and Harrison[6]. While larger samples increase the time required for washing and filtering, it is the authors' experience that greater accuracy and reproducibility are attained thereby. Jacob Gabry, to whom the authors are indebted for the analytical results reported here, also points out that it is essential to control the time of digestion of the rubber stock and nitric acid to 3 to 4 hours at the specified temperature of 60° to 70° C. While in the case of channel blacks, the weight of carbon black recovered by this method is generally reported[6] to be 105 per cent of its original weight, under the conditions reported here a value of 108 per cent has been found more general. Consequently, a correction factor of 1.08 is employed instead of the value 1.05 recommended by Oldham and Harrison[6].

One to 0.75 gram of vulcanized stock was digested for one hour with 15 cc. of concentrated acid. After the addition of another 35 cc. of acid, digestion was continued for 2 hours more. To avoid contamination of the black for the subsequent surface-area determination, a Selas sintered filter crucible FS-20-100 was used in place of the usual asbestos Gooch. The crucible and black were washed according to the standard method, then dried at 110° for 2 hours. The per cent carbon in the rubber stock was determined directly without ignition. The surface area of the dried sample of recovered black was then determined by low-temperature nitrogen adsorption. The ash was determined on a duplicate sample by ignition. In all compounds studied, it amounted to about 0.4 per cent by weight of the whole rubber stock. Thus the recovered black as weighed out for the surface-area determination contained 1.44 per cent ash. The surface values in column 4 of Table I are accordingly 1.44 per cent lower than if they had been calculated on ash-free basis. However, in the absence of data on the surface-area of ash itself, such a simple correction is not justified. The correction in any case would not amount to more than 1 or 2 square meters per gram, a value too small to cause any confusion in the identification of the black.

It was necessary to establish that no appreciable change in surface area of the carbon black was brought about by nitric acid during separation of the

black from the rubber stock. To establish this, "blanks" of 0.5-gram samples of carbon black alone were subjected to the same treatment employed with the compounded rubber stock, and the surface areas of the blacks were then determined.

The use of cresol for the separation of carbon black from rubber stocks has been described by Roberts[7]. In natural rubber stocks, this method gives excellent results for free carbon. It was felt that there would be less opportunity for alteration of the carbon surface during separation by this method than with concentrated nitric acid. The carbon black was separated from the stocks by cresol, according to the method of Roberts[7]. The surface-area of the recovered carbon was then measured.

A single determination of the area of a Grade-6 carbon black recovered from a Buna-S stock with nitric acid was carried out. As it was not possible to get complete solution of this stock in cresol, the method had to be abandoned in this instance.

EXPERIMENTAL RESULTS

Table I presents a summary of the data collected. With the exception of Gastex and Grade-9 channel black, which are values for single recoveries, the surface-area values reported are the average of at least two independent recoveries. The deviation in all cases was not more than 3 per cent.

TABLE I

EXPERIMENTAL RESULTS

Black	Original area	Area after treating with HNO_3	Area after recovery from rubber		Carbon in rubber		
			By HNO_3	By cresol	HNO_3 method	Cresol method	Carbon calculated
	Sq. m./g.	Sq. m./g.	Sq. m./g.	Sq. m./g.	%[b]	%	%
Gastex	26[a]	...	22	21	28.4	27.7	27.8
Acetylene	64	67	63	70	...	...	...
Cabot grade 9	99	...	100	99	27.8	27.2	27.8
Cabot grade 6	109	112	110	107	27.7	27.4	27.8
Cabot grade 4	143	181	175	125	27.9	27.7	27.8
Cabot grade 1	210	...	203	156	28.1	27.7	27.8
Spheron N	330	316	326	204	...	...	...
Grade 6 in Buna-S	109	...	113	...[c]	29.9	...	30.3

[a] A previous publication[2] reported 40 sq. m. per gram as the surface of standard Gastex. C. W. Snow, General Atlas Co., has kindly stated that this material was actually CS-3 carbon. The present value is that of standard Gastex.
[b] Ash-free basis.
[c] Not completely soluble.

The data indicate that carbon black undergoes no appreciable alteration in surface-area during incorporation in, or vulcanization of, a rubber stock. With but a single exception, the surface-areas of the carbon blacks studied are substantially the same before incorporation and after removal from the rubber stock by means of nitric acid.

It is not possible to offer any ready explanation for the 25 per cent increase in surface of the Grade-4 sample. This is not due to any peculiar effect of the rubber on the carbon black, since the black alone in nitric acid showed an appreciable increase in surface. There was nothing peculiar in the method of manufacture or properties of this particular sample to account for its apparent increased activity toward nitric acid. In any case, the alteration in the surface-area of the recovered carbon is still not sufficient to confuse its identity.

In general, both the nitric acid and cresol methods gave excellent results for the amount of free carbon in the stocks. The surface-areas of the blacks recovered by the cresol method show satisfactory agreement with the original supply in the case of the coarser blacks. However, with the finer particle blacks, the surface is considerably reduced. Thus, Grade-1 black has an original surface of 210 square meters per gram. After recovery from the tread stock by cresol extraction, this value was only 156. After treating a 0.5-gram sample of this type black with cresol according to the standard procedure, the surface was 165 square meters per gram. Evidently a small amount of material is retained by the carbon in spite of the extensive washings and heating described in the procedure. The amount is not sufficient to alter the weight of the sample appreciably, but it is sufficient to block off certain interspaces in the black that were formerly accessible to the nitrogen molecule. Such an effect should become more pronounced the finer the particle size of the black. Accordingly, the cresol method of recovery is not satisfactory for separating carbon black from "unknown" rubber stocks for identification by surface-area measurements.

The Buna-S stock showed little solubility in cresol, and quantitative recovery of carbon was not possible. It was possible, however, to get a satisfactory recovery of carbon from the Buna-S stock with nitric acid. To obtain complete solution, it was necessary to digest this stock with nitric acid somewhat longer than the specified 3 hours. This more drastic procedure is reflected in the slight increase in surface area of the recovered carbon.

CONCLUSIONS

In general then, we may conclude that carbon black can be recovered from rubber stocks with unchanged surface-area. The nitric acid technique is the most effective method of effecting the separation. The digestion temperature must be controlled to between 60° and 70° C, for a total of not more than 3 to 4 hours. This method of identifying the carbon black in an unknown rubber stock is directly applicable only in the presence of a single type of carbon black. If blends of blacks are employed in the material under investigation, some secondary identification is also required. The nonimpingement-type blacks, for example, are readily identified by microscopic observation. From the known surface-areas of these materials and the total per cent carbon present in the stock, a fairly positive identification of the blend can be made.

The fact that carbon black can be recovered quantitatively and with unchanged surface-area from vulcanized rubber stocks appears to lend impetus to a physical concept of carbon black reinforcement. This point of view implies that any chemical combination between the ingredients of the rubber stock and the carbon black would be evidenced by some alteration in the surface of the latter. A few experiments were performed in an attempt to establish to what extent this concept was valid.

One hundred grams of Grade-6 carbon black were intimately mixed with 6.6 grams of sulfur. This is about the ratio in which they are present in a standard rubber batch. Samples of this mixture were subjected to the standard curing temperature of 134° C for 30, 60, and 90 minutes. The free sulfur was then extracted for 40 hours with acetone and the combined sulfur on the carbon was determined. Values of 0.16, 0.21, and 0.4 per cent combined sulfur were obtained. The original sample of Grade-6 carbon black had a surface-area of 108 square meters per gram. The extracted sample of black

containing 0.4 per cent of combined sulfur had a surface-area of 109 square meters per gram. These values are identical within experimental error.

While unaltered surface-area need not necessarily be interpreted as evidence of complete lack of surface reactions, it is the authors' opinion that the extent of chemical combination at the carbon black surface is very small. This interpretation is in accord with the views expressed in a previous publication[3], where it was suggested that the chief role of carbon black in rubber reinforcement may rest on its ability to orient the chains of rubber molecules[9] and thus alter the extent and type of rubber-sulfur bonds normally formed in non-reinforced rubber stocks.

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LOW TEMPERATURE FLEXING APPARATUS *

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For the past ten months, Sub-Committee V of SAE-ASTM Technical Committee A on Automotive Rubber has been working on the standardization of synthetic rubber specifications. Insofar as possible, methods of tests have followed ASTM procedures. ASTM has no recommended procedure for measuring the low temperature flexibility of synthetic rubber. This committee, after careful consideration, has recommended the use of a modification

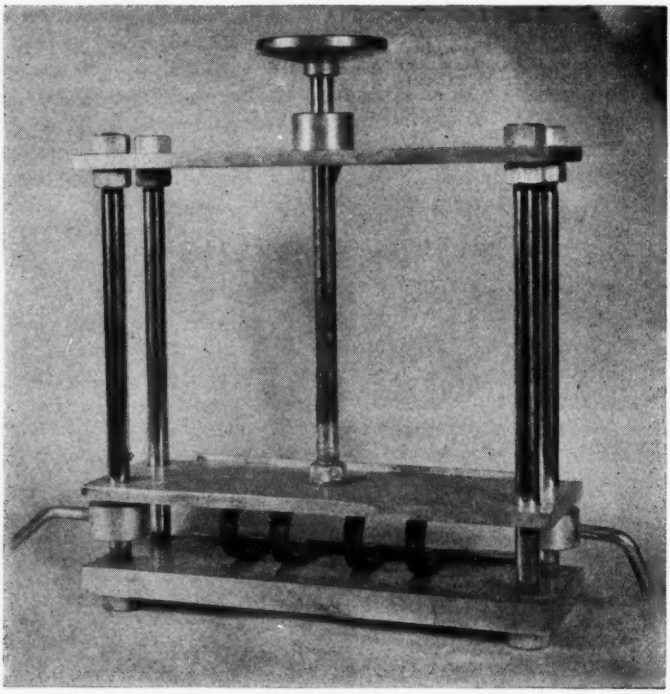

FIG. 1.—A modification of the Thiokol apparatus as used in the Chrysler Laboratories.

of the Thiokol Corporation's freeze test. This method of testing for low temperature flexibility has been incorporated into a number of recent Aeronautical Material Standards Specifications covering synthetic rubber.

The modified test uses the same apparatus as that used in the Thiokol Corporation's Laboratory, or slight modifications of this. Because of the interest in this apparatus, a short description of it is here given.

The instrument and its operation can best be understood from the accompanying photographs. The picture shows the instrument mounted on the top

* Reprinted from *The Rubber Age* (New York), Vol. 52, No. 3, pages 227–228, December 1942.

of the cold box. This has been removed from the box for the purpose of photographing. The principle of the test is based on bending the samples between two parallel plates. By controlling the minimum distance between the plates at the time of maximum bend, the sample can be given almost any desired radius of bend. By turning the crank, the samples are flexed. Whether

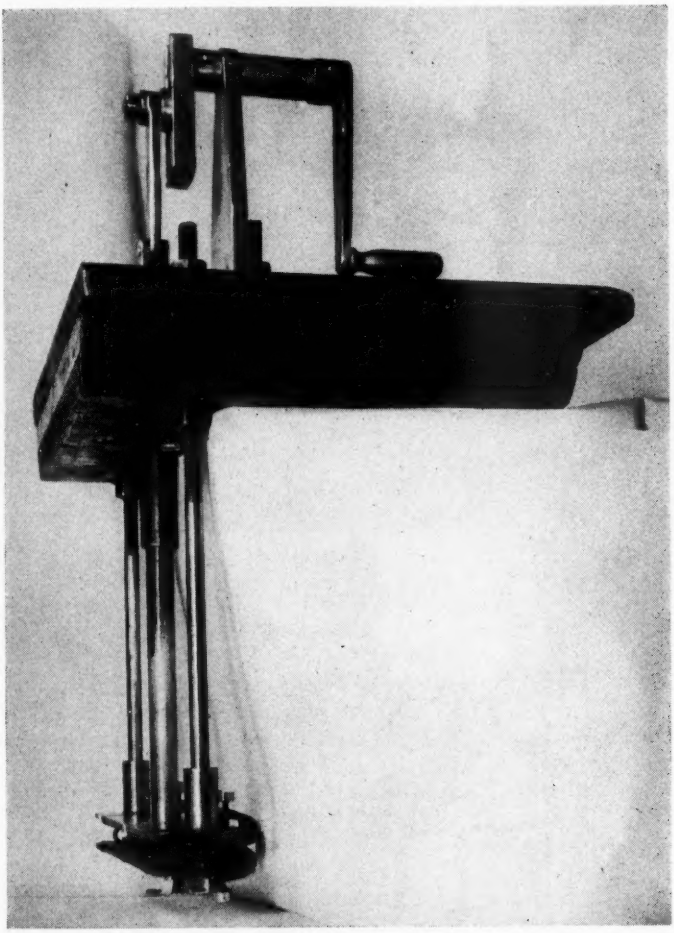

FIG. 2.—Samples mounted in the apparatus with plates apart preparatory to flexing.

the crank is turned a half revolution, a whole revolution, or several revolutions, depends on the prescribed conditions set up for the test.

The sample, which is usually in the form of a strip 4″ × 0.25″ × 0.60″, is mounted between plates 2½″ apart to form a loop. The plates should be sufficiently wide (*i.e.*, 2″ to 2½″) so that the bend in the test piece does not protrude beyond the edge when the plates are brought together.

When the samples have been properly conditioned at the low temperature, the samples are flexed by simply turning the crank.

The apparatus is very simple and exceedingly flexible. It allows numerous adjustments as to the amount of bend given the sample, and also the number of bends.

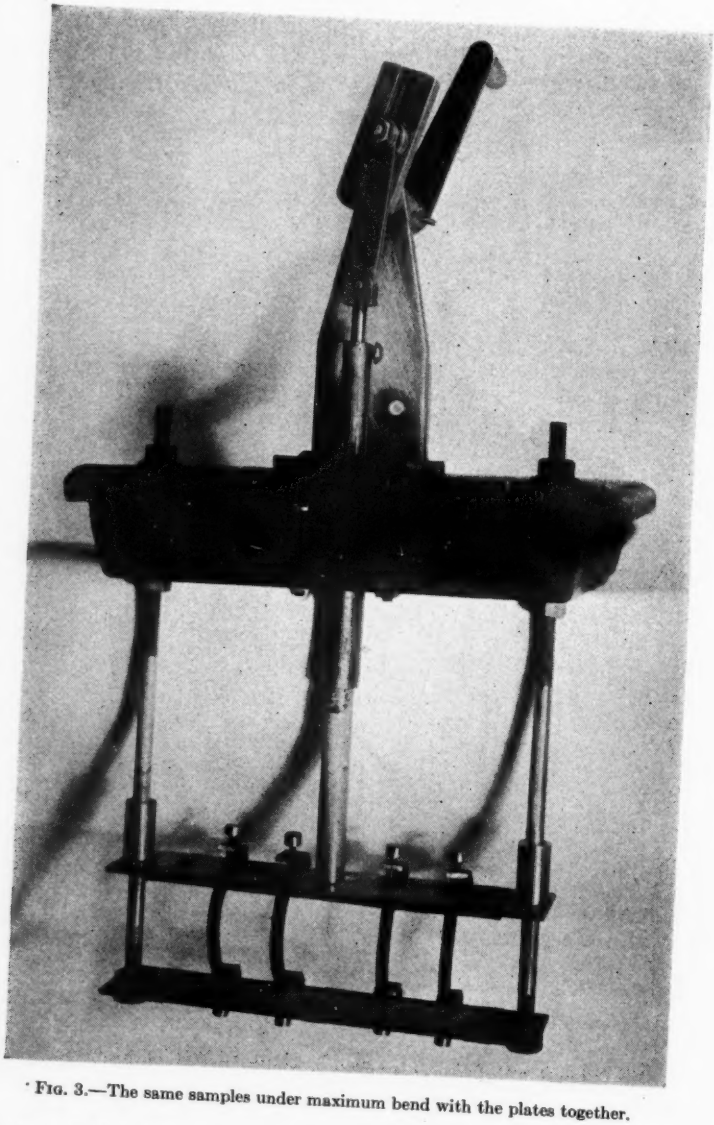

FIG. 3.—The same samples under maximum bend with the plates together.

A number of these instruments have been made without the crank. Here the movement is activated by pushing down on a rod attached to the top plate.

A modification used in the Chrysler Laboratories is shown in an accompanying photograph.

A BROAD NOMENCLATURE FOR CARBON BLACKS *

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The introduction of new carbons for use in rubber and the application of established grades to new uses has led to a confusing terminology. Perhaps it should be said that lack of terminology has led to confusion.

Since entry of the United States into the War, reclaimed rubber has been used more generously in tires, including tread stocks, to extend the natural rubber stockpile. This has brought about a considerable use of black of the impingement channel type, which is slightly coarser and somewhat less reenforcing than that previously employed in tire treads. The grade in question has long been available for specialized uses, and has been referred to within the carbon industry as "soft channel black". However, it is unfortunate that rubber compounders have more recently come quite frequently to refer to this type simply as "soft black". Intermediate carbons not made by the channel process are now receiving wide attention. These, and a large group of already established grades, are distinctly coarser than the softest channel black, so it is a matter of some importance to exercise care in the nomenclature.

THERMAL FURNACE-PROCESS BLACK

The rubber pigment which has longest and most properly been referred to as "soft black" is that made in a furnace by a thermal decomposition process which accomplishes direct cleavage of the hydrocarbon molecule. The first carbon of this class to be developed has a particle diameter of 274 mμ, and one pound has a surface area of about one acre. This and others of the same category are extenders rather than reënforcers, and the term "soft carbon" supplies an apt description from the point of view of the compounder. The term "*coarse thermal carbon*" would be technically more accurate, and general use of this designation is suggested.

Fine thermal furnace black.—Modification of this process involving gas dilution produces a much finer black (P-33), with particle diameter of 74 mμ. Characterized by tensile strength and tear resistance in natural rubber approaching the reënforcing blacks, but differing sharply by developing low modulus compounds, this type is sometimes referred to as "low modulus black". "*Fine thermal black*", however, affords a better description.

COMBUSTION FURNACE-PROCESS BLACK

As far back as the early '20s, gas carbon black was produced in a furnace by combustion of natural gas with controlled access of air. This procedure differs essentially from the furnace method described above in that the latter involves a thermal surface action to crack the hydrocarbon molecule; whereas the furnace process employed to produce semi-reënforcing carbons depends on flame. Hydrogen is the byproduct of the thermal process, but the through gases are oxides of carbon and water in the combustion operation. Although following the essential flame chemistry of the channel procedure, the com-

* Reprinted from the *India Rubber World*, Vol. 107, No. 4, page 378, January 1943.

bustion furnace method differs radically in that, on account of the size of the flame, collection by means other than impingement is necessary.

A typical carbon of this group is Furnex. The particle diameter of 83 mμ is only very slightly coarser than the 74 mμ diameter of P-33, and the surface area of this group averages in the neighborhood of four acres per pound. This type is outstanding because it combines important reënforcing effect with high resilience.

Semi-reënforcing black.—This is an accurate description—much better to use than "furnace black", both because the thermal blacks actually are also furnace blacks and because intermediate types also may be produced by furnace processes. It is a good practice to refer to this type by the convenient abbreviation *"S.R. Carbon"*.

CHANNEL IMPINGEMENT-PROCESS BLACK

The particle sizes of commercial grades which enjoy large-volume use in industry range from an average diameter in the neighborhood of 30 mμ all the way down to 13 mμ. Surface area provides an even better point of view for consideration of the rubber grades which range from 10 to 12 acres per pound. Specialty grades used for ink and paint range up to 22 acres; the latter figure corresponds to the particle diameter of 13 mμ. Having regard for these basic physical differences, it is clearly evident that no black in this category should ever be referred to as a "soft type".

Although several individual producers of impingement channel black now offer a range of grades for rubber which embrace one-half dozen or more separate types, there are three main groups which (if specialties are excepted) account for practically all material of the channel category used in rubber. These are: (1) the finer extra reënforcing, (2) the standard reënforcing, and (3) the coarse or easy processing type.

These can well be distinguished on the basis of available surface area, considering the extra reënforcing type as a *"fine channel"* black, since it has a surface area in the neighborhood of 11½ acres per pound. The standard reenforcing type might then be classed as *"medium channel"* black, based on its surface area of from 10½ to 10¾ acres per pound. Material of clearly coarser particle size, for example, such as possesses a surface area of not more than 10.3 acres per pound, could properly be distinguished for the other grades by the designation *"coarse channel"* black. On the basis of the foregoing discussion the following line-up is suggested:

Type (Carbon pigment)	Surface (Acres per pound)	Examples
Coarse thermal	1.0	Thermax, Shell, etc.
Fine thermal	4.0	P-33
Semi-reënforcing ("S.R.")	3.5–4.0	Furnex, Gastex, etc.
Channel impingement		
Coarse channel	10.3 or less	Micronex W-6, etc.
Medium channel	10.5–10.75	Standard Micronex, etc.
Fine channel	11.5–12.0	Micronex Mark II, etc.

An additional type: namely, special reënforcing furnace carbon, as represented by Statex, is assuming more and more importance. It is, of course, more difficult to employ broad terms when referring to carbons produced by special means, particularly where available types are distinctly unique and

exhibit individual characteristics. On the other hand, where several brands fall into clean cut groupings, a generic nomenclature can be developed.

General use of the suggested designations throughout the trade would materially assist in proper discrimination between broad types. Use of such generic terms in service literature of suppliers of other raw materials is desirable from every point of view.

BUNA FOR HARD RUBBER LININGS

E. GARTNER

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RUBBER CHEMISTRY AND TECHNOLOGY contains, on pages 899–913 of the October 1941 issue, an article with the title above. Attention has been called by the Intelligence Officer of the Research Association of British Rubber Manufacturers to certain errata and desirable improvements, some of which are attributable to corresponding errata in the original German Journal, others of which are traceable to the translation.

For the enlightenment and benefit of the reader and user of this article by Gartner, these errata are itemized below.

Page 899 Under section (2) of the table, the proportion of sulfur should read 26–38, not 26–28.

900 The legend under Figure 2 gives no proportional parts for Buna-85. This should read Buna-85 100.

901 In the legend under Figure 3, Buna-SS should be Buna-S.

906 In the legend under Figure 7, Buna-85 should be Buna-S.

907 At the top of Table III, the first bracket (for Natural Rubber) should embrace 1, 2, 3, and 4; the second bracket (for Buna-85) should be embraced by only 5 and 6.

911 In Table IV, the last two items (Buna-S and Oppanol) should be bracketed together, the note after Oppanol (calculated on rubber) should be eliminated, and the numbers of the mixings should be 19 and 20, not 25 and 26. In next to the last line of page 911, Buna-SS should be Buna-S.

912 In Table V, sixth column (column headed (1) under tan δ), the ninth value down the column should read 0.0114, not 0.0014. In the last column, the sixth and seventh values should read 3.1 and 3.0, not 2.9 and 2.9.

913 In the fifth line, "Buna-S" should read "Buna-85", and "Buna-SS" should read "Buna-SS and Buna-S". In the table headed "CHEMICAL STABILITY", "Natural rubber" appears twice unnecessarily in the second column under "Hydrochloric acid". In the same table, the item "Sulfuric acid (dilute)" should be followed by "Sulfuric acid (concentrated)". For this, the second column ("Very satisfactory") should read "Only blends of Buna-S or Buna-SS with Oppanol show even fair stability"; the third column ("Unsatisfactory") should read "All other vulcanized materials". In the same table, the item "chlorine gas" should designate as "Very satisfactory" "Buna-85 vulcanized in steam and Neoprene" instead of only "Buna-85 vulcanized in steam".

In the last paragraph of the article, there is possible ambiguity. The meaning is that natural rubber and Buna-SS are about equal as insulators; Perbunan and Perbunan-extra are the poorest insulators because they are semi-conductors.

ELECTRICAL PROPERTIES OF NEOPRENE *

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E. I. DU PONT DE NEMOURS & COMPANY, INC., WILMINGTON, DEL.

This review is based on data selected from tests conducted over a period of years. Under the circumstances it does not happen that identical Neoprene was used throughout. Several types are referred to in the compounds. Each group of tests is consistent within itself, but direct comparison from group to group is not justified. Neither do exact values within a group have individual merit, but the trends of electrical quantities with controlled changes of the variable under study are of primary importance. In general, numerical values reported are the average of results obtained on two samples, but all conclusions have been confirmed by numerous parallel and related tests.

Unless otherwise specified, tests were made at 82° F, after the samples had been dried in a desiccator for at least 16 hours. Conventional methods[2] were used. For all tests except those on dielectric strength, tinfoil electrodes 0.001 inch thick, adhered to the test slab by a thin film of petrolatum, were utilized. The test-specimens were usually $6 \times 6 \times 0.075$ inch, except for occasional samples which were approximately 0.020 inch thick. In the case of the direct-current resistivity test, the upper electrode was a 3-inch-diameter disk of tinfoil surrounded by a guard ring. The lower electrode was a 6-inch square of tinfoil. The Leeds & Northrup test set consisted of a sensitive galvanometer and an Ayrton shunt. An alternating-current bridge was used for measurements of conducting stocks. For the tests of power factor and dielectric constant, the upper electrode was a 3-inch-diameter disk of tinfoil, without a guard ring. The lower electrode was a 6-inch square of tinfoil. General radio equipment was utilized, consisting of a type-716A capacitance bridge, complete with the necessary auxiliaries. A telephone headset was used for detection of null points. All tests reported here were conducted at frequencies of 1000 cycles per second.

For the determination of dielectric strength, an American Transformer Public Utility test set, type-TS, having a secondary voltage range from 100 to 50,000 volts was used. The electrodes were of the standard A.S.T.M. type[3]. Ordinarily the test-specimens were about 0.020 inch thick and 6 inches square. The voltage across the electrodes was gradually increased until breakdown occurred. The gauge was then measured adjacent to the punctured spot, and the voltage and dielectric strength were calculated by dividing the value of the voltage by this gauge.

EARLY DATA

Early published information on the electrical properties of Neoprene appeared in 1936[4]. Results from this report are given in Table I.

It is immediately evident that the resistivities of all three compounds were distinctly low in comparison with that of rubber insulation, which ordinarily has a value approximating 10^{15} ohm-cm. Also, the dielectric constant for all three compounds was high in comparison with that for most rubber insulation.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 35, No. 3, pages 330–335, March 1943. This paper was presented before the Division of Rubber Chemistry at the 102nd Meeting of the American Chemical Society, Atlantic City, N. J.

TABLE I

EARLY DATA ON THREE NEOPRENE COMPOUNDS

Compound No.	750D–1	750D–3	750D–5
Neoprene (Type E)	100	100	100
Extra-light calcined magnesia	...	10	2
FF wood rosin	...	5	10
Phenyl-β-naphthylamine	...	2	2
Sulfur	...	1	1
Zinc oxide	...	10	...
Litharge	...	...	20
Cure at 307° F (min.)	60	20	20
Electrical properties			
D.C. resistivity (ohm-cm.)	2.2×10^9	3.1×10^{11}	9.0×10^{11}
Dielectric constant	8.2	7.3	7.2
Dielectric strength (volts per mil)	380	860	720

Both of these trends were distinctly unfavorable from the standpoint of insulation. On the other hand, the values for dielectric strength, except for uncompounded vulcanizate 750D–1, were roughly comparable with rubber. The results make it desirable to survey the possible methods of improving the electrical properties of Neoprene which follow:

1. Compounding with litharge.
2. Purifying the crude Neoprene.
3. Including carbon black in the formula as an absorber for electrolytes.
4. Including large amounts of superior insulating substances.
5. Mixing with rubber insulation to provide a compromise between the electrical properties of rubber and the superior mechanical and chemical properties of Neoprene.
6. Conditioning treatments of vulcanized Neoprene to improve its electrical properties.
7. Adjusting the cure.
8. Modifying the Neoprene polymer.

COMPOUNDING WITH LITHARGE

Litharge is superior to magnesium oxide and to zinc oxide as a curing agent for Neoprene insulation. For example, the data of Table I show a pronounced difference in favor of litharge. It is probable that the reaction between litharge and the degradation products of Neoprene forms salts with lower dissociation constants in the presence of moisture than have the corresponding salts of zinc and magnesium. The higher resistivity of litharge compounds is attributed primarily to this factor. In addition to the advantage of litharge electrically, Neoprene compositions containing it are definitely less combustible than compositions containing zinc oxide.

PURIFICATION OF CRUDE NEOPRENE

As various tests have shown, the amounts of chlorine-bearing electrolytes that might be suspected in normal Neoprene compounds are difficult to detect by chemical means. Yet the possibility remains that they may be present in sufficient amount to cause the inferior electrical characteristics of untreated Neoprene. With this possibility in mind, a sample of Neoprene Type E was extracted by acetone and then washed with water. This specially purified

Neoprene was compounded and tested for electrical characteristics in the following formula:

COMPOUND 1333N–112

Purified Neoprene (Type E)	100
Extra-light calcined magnesia	3
FF wood rosin	5
Sulfur	1
Phenyl-α-naphthylamine	2
Litharge	20
D.C. resistivity (ohm-cm.)	2.8×10^{13}
Dielectric constant	7.8
Power factor (percentage)	1.25

The improvement in resistivity as the result of purification was substantial; it was also suggested by Kemp[5]. Although the dielectric constant was not greatly changed, the power factor was relatively low in comparison with contemporary tests of unpurified Neoprene specimens. Washing with acetone, however, is not practical from a production standpoint and, at the time of these tests, it could only be hoped that advances in the technique of Neoprene production would result in improved electrical properties.

INCLUSION OF CARBON BLACK

The practice with certain types of rubber insulation is to include moderate amounts of carbon black in the formula as an absorber for impurities and electrolytes[6]. The possibility of following a similar procedure for Neoprene was investigated in the stocks shown in Table II.

TABLE II

EFFECT OF CARBON BLACK ON FORMULA 1333N (CURED 40 MINUTES AT 307° F)

Formula 1333N–	87	88	89	90	91
Neoprene (Type E)	100	100	100	100	100
Extra-light calcined magnesia	3	3	3	3	3
FF wood rosin	5	5	5	5	5
Semireinforcing black	...	3	10	20	30
Phenyl-β-naphthylamine	2	2	2	2	2
Sulfur	1	1	1	1	1
Litharge	20	20	20	20	20
Electrical properties of dry slabs					
D.C. resistivity (ohm-cm.)	4.9×10^{11}	5.2×10^{11}	6.3×10^{11}	6.4×10^{11}	6.5×10^{11}
Dielectric constant	7.74	8.43	9.72	13.28	17.33
Power factor (percentage)	2.1	2.0	2.1	2.8	4.1
Loss factor	0.16	0.17	0.20	0.39	0.71

Although the improvement in power factor and resistivity is slight for the compound containing 3 parts of carbon black, the trend appears to be favorable. On the other hand, the dielectric constant increased and, as a consequence, the loss factor increased by the inclusion of even this small amount of carbon black. For ordinary applications of insulation, the loss factor is not of prime importance. It may be preferable in many cases to make a sacrifice with respect to loss factor to increase the value of the resistivity. However as the quantity of black is increased, the loss factor increases out of all proportion to the gain in resistivity. As a consequence, it appears advisable to limit the carbon black content of insulating compounds to about 5 parts of carbon black.

TABLE III

EFFECT OF INSULATING MATERIALS ON FORMULA 1333N (PRESS-CURED 40 MINUTES AT 307° F)

Formula 1333N–	200	201	202	203	204	205	206	207	208
Neoprene (Type E)	100	100	100	100	100	100	100	100	100
Extra-light calcined magnesia	10	10	10	10	10	10	10	10	10
FF wood rosin	5	5	5	5	5	5	5	5	5
Whiting	...	...	...	118	...	...	...	...	...
Barytes	...	...	...	...	194	...	...	...	...
Crown clay	...	...	113	...	...	...	...	...	...
Cottonseed oil	...	...	...	...	...	20	...	...	...
Mineral rubber	...	...	...	...	...	...	50	...	...
Mineral oil	...	...	...	...	...	...	...	20	...
Paraffin	...	...	...	...	...	...	...	...	10
Phenyl-β-naphthylamine	2	2	2	2	2	2	2	2	2
Neophax B[a]	...	100	...	...	...	...	...	...	...
Zinc oxide	10	10	10	10	10	10	10	10	10
Electrical properties after 13 days in desiccator at 25° C									
D.C. resistivity (ohm-cm.)	1.7×10^{11}	8.2×10^{11}	3.1×10^{12}	6.3×10^{11}	4.7×10^{11}	9.3×10^{10}	1.1×10^{12}	2.8×10^{11}	7.5×10^{11}
Dielectric constant[b]	7.88	6.62	8.40	8.67	8.56	7.10	5.88	6.62	7.20
Power factor[b] (percentage)	3.8	2.6	3.4	3.0	2.4	4.4	2.4	3.0	3.5
Loss factor[b]	0.30	0.17	0.28	0.26	0.20	0.31	0.14	0.19	0.25

[a] A special grade of factice (vulcanized oil).
[b] At 1000 centipoises.

TABLE IV

ELECTRICAL PROPERTIES OF NEOPRENE-RUBBER MIXTURES

Formula 1333N–	1333N–210	1333N–211	1333N–212	1333N–213	1333N–214	1333N–215	1333–50
Neoprene (1333N–210)	100	95	75	50	25	5	...
Rubber (1333–50)	...	5	25	50	75	95	100
Electrical properties							
D.C. resistivity (ohm-cm.)	6.6×10^{12}	8.0×10^{12}	9.0×10^{12}	2.9×10^{13}	2.4×10^{14}	9.4×10^{14}	9.4×10^{14}
Dielectric constant	8.2	8.14	7.36	6.41	5.94	5.05	5.03
Power factor (percentage)	1.3	1.2	1.3	1.2	0.9	0.5	0.5
Loss factor	0.106	0.098	0.095	0.077	0.053	0.025	0.025

INCLUSION OF INSULATING MATERIAL

The effect of various materials is shown in Table III, based on Neoprene Type E compounded with magnesium oxide and zinc oxide. Although higher values for the resistivity would have resulted by compounding with litharge, it was thought that the effects of the fillers would be demonstrated at least as well in the zinc oxide formulation. The inorganic fillers were compared on an equal basis of 40 volumes per 100 volumes of Neoprene. The organic fillers were used in amounts approaching the maximum permissible in a practical formulation.

Control formula 1333N–200 is inferior in all insulating properties with the exception of one value for resistivity, three for dielectric constant, and one for power factor. In a general way it is interesting to note that the d.c. resistivity is increased by compounding with inert, inorganic fillers, but that these increase the dielectric constant. All other materials except cottonseed oil increase the d.c. resistivity, decrease the dielectric constant and power factor. It is possible that the cottonseed oil used in this test was of an inferior grade electrically and that the results are not necessarily typical of this processing material. It is also obvious that, with the exception of the stock containing cottonseed oil, the loss factor for all compounds is lower than that of the control stock.

INCLUSION OF NATURAL RUBBER

Rubber itself is a possible compounding ingredient for Neoprene, and the following two compositions were blended by weight in the amounts indicated in Table IV to determine its possibilities. Slabs were press-cured 40 minutes at 287° F:

Compound 1333N–210		Compound 1333–50	
Neoprene (Type GW)	100	Smoked sheet	100
Catalpo clay	100	Zinc oxide	78
Blanc fixe	100	Gilder's whiting	115
Medium-process oil	5	Phenyl-α-naphthylamine	2
Cottonseed oil	5	Paraffin	5
Semireinforcing black	5	Litharge	10
Paraffin	5	Accelerator[a]	0.4
Phenyl-β-naphthylamine	2	Sulfur	3
Litharge	20		

[a] 90% zinc salt of mercaptobenzothiazole and 10% di-o-tolylguanidine.

The results indicate a progressive improvement in insulating properties as the percentage of rubber is increased. On the other hand, the improvement is most rapid for rubber contents of more than 50 per cent. There may be many possibilities in the future for insulating mixtures of Neoprene and rubber, where greater resistance is required to heat, sunlight, oil, and flame than is possible with rubber alone. The advantages of Neoprene are gradually lost, however, as the percentage of rubber is increased, and the present mixtures with rubber appear to be an impractical way of improving the electrical properties of Neoprene.

CONDITIONING TREATMENTS

Three practical compounding approaches to the insulation problem are offered by the foregoing. They are inclusion of carbon black, activation with litharge, and inclusion of proper insulating materials. The combination of these principles in a practical formula for wire insulation is exemplified by the following composition:

Compound 1333N–209	
Neoprene (Type GW)	100
Blanc fixe	100
Catalpo clay	100
Paraffin	3
Medium-process oil	5
Semireinforcing black	5
Phenyl-β-naphthylamine	2
Litharge	20

Compound 1333N–209 was extruded as 3/64-inch wall insulation No. 14, solid AWG tinned copper wire; the following history of resistance per 1000 feet of wire indicates possibilities in conditioning treatments for Neoprene-insulated wire:

Step No.	Treatment	Temp. (° C)	Megohms per 1000 Ft.
1	Original immersed in water	29	13.5
2	After 24-hr. immersion	29	2.8
3	Plus 30 min. at 1500 volts	29	9.2
4	Total immersion 44 hrs.	29	3.8
5	44-hr. immersion + 3.5 hr. at 1500 volts	29	10.4
6	17-hr. drying in 70° C oven	24	44.0
7	Plus 4.5 hr. at 1500 volts after oven-drying	24	32.9

It is recognized that rubber insulation, which is slightly low in resistivity, can be improved by subjecting it to high voltage for a time without detracting from the other desirable insulating properties. The preceding data on Neoprene insulation show that extensive exposure to high voltage likewise increases its resistance. It is also significant that the initial period of immersion caused a severe drop in the resistance per thousand feet of wire, while the trend after continued immersion and extensive exposure to high voltage was to restore the d.c. resistivity almost to its initial value. The highest value attained after 17 hours of drying in the 70° C oven was probably the combined result of reduction in moisture content and of tighter cure. Although these results would not be considered typical of any normal test procedure, they indicate gradual improvement of electrical properties under severe conditions and are reassuring from a service standpoint.

ADJUSTMENT OF CURE

A further possibility with respect to electrical properties is adjustment of cure. The following data illustrate the idea that more extensive knowledge of compounding principles for Neoprene may result in superior electrical properties, even with the present types of Neoprene. The data also indicate the stability of the electrical properties of Neoprene under severe aging conditions. The compounds compared (cured 30 minutes at 40 pounds) are as follows:

Compound No.	1333N–216	1333N–217
Neoprene (Type GN)	100	100
Hexamethyleneammonium hexamethylenedithiocarbamate	...	0.25
Paraffin	5	...
Phenyl-β-naphthylamine	2	...
Semireinforcing black	5	...
Catalpo clay	100	...
Blanc fixe	100	...
Medium-process oil	10	...
Litharge	20	...

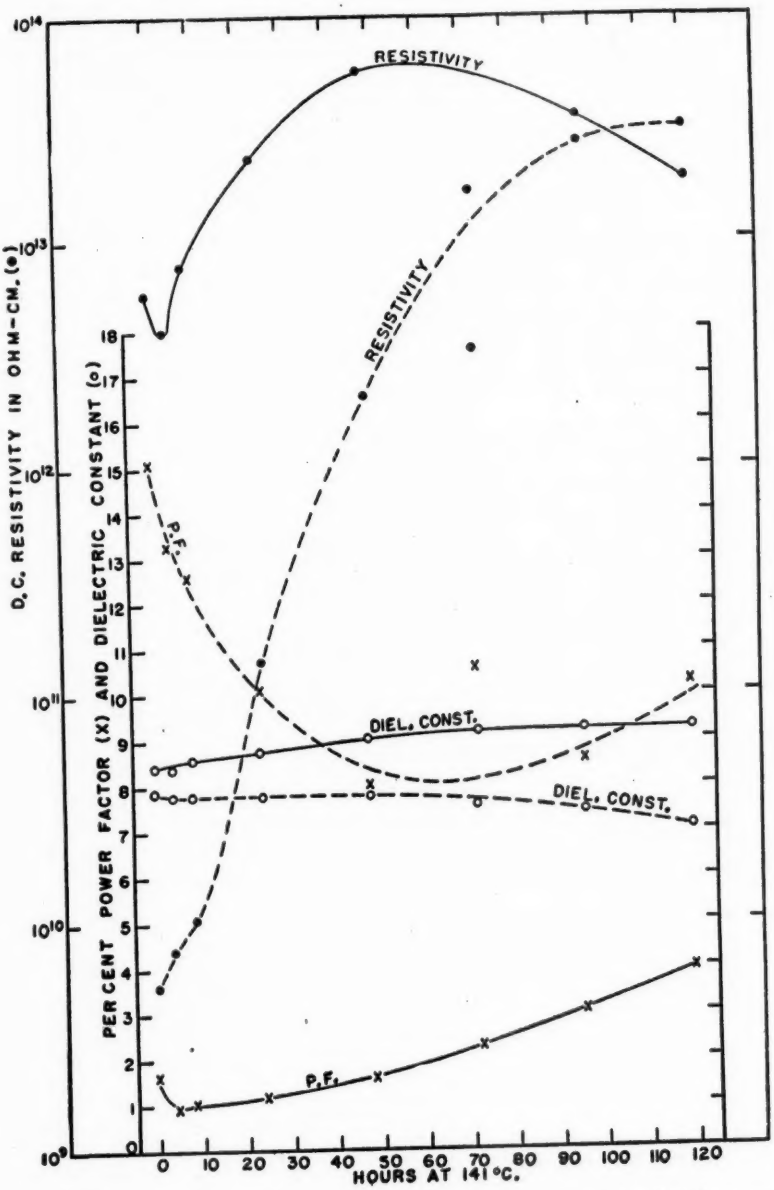

FIG. 1.—Comparison of stocks, compounded (solid curves) and uncompounded (dotted curves).

Measurements were made of d.c. resistivity, dielectric constant, and power factor after aging for various intervals in a 141° C oven. The trends of these various quantities for the two compounds are shown in Figure 1. Comparison of the resistivity curves for the compounded and uncompounded stocks indicates conclusively that neither was cured to its maximum effectiveness electrically as originally prepared. The maximum attained by the compounded sample after 48 hours was 5.7×10^{13} ohm-cm.; that attained by the uncompounded specimen after 120 hours was 3.2×10^{13} ohm-cm. The discrepancy between the two may be the result either of the difference in state of cure or of the presence of insulating extenders in the compounded stock. Also, the dielectric constant of the uncompounded material is lower at all points than that of the compounded material. In percentage power factor, the compounded stock is definitely superior at all aging intervals to that of the uncompounded stock, although it appears possible that a longer exposure at 141° C might bring these two values together. On the other hand, the uncompounded material had become hard and brittle by the end of 121 hours, and more extensive exposure would not have been practical.

MODIFICATION OF THE POLYMER

The history of Neoprene is a series of eventful improvements in physical properties. Thus, as a further possibility it can be expected that future modifications of Neoprene will have electrical properties vastly superior to those displayed by current types. Neoprene Type-FR, the latest addition, shows interesting possibilities:

Compound No.	1333N–218	1333N–219
Neoprene (Type FR)	100	...
Neoprene (Type GN)	...	100
Piperidine pentamethylenedithiocarbamate	...	0.1
Phenyl-α-naphthylamine	2	2
Blanc fixe	100	100
Clay	100	100
Semireinforcing black	5	5
Process oil	10	10
Paraffin	5	5
Litharge	20	20
Cure at 287° F (min.)	40	30
Stress at 300% (lbs. per sq. in.)	275	550
Stress at 500% (lbs. per sq. in.)	425	650
Tensile strength (lbs. per sq. in.)	700	1125
Elongation at break (percentage)	950	810
Hardness	44	67
Electrical properties		
D.C. resistivity (ohm-cm.)	1.2×10^{13}	4.2×10^{12}
Power factor (percentage)	0.9	1.6
Dielectric constant	7.3	8.3
Loss factor	0.066	0.12

EFFECT OF TEMPERATURE ON RESISTIVITY

The effect of temperature upon the resistivity of Neoprene is indicated by the following compound and data:

Compound 1333N-220

Neoprene (Type GN)	100
Piperidine pentamethylenedithiocarbamate	0.25
Phenyl-β-naphthylamine	2
Gastex (carbon black)	5
Ground mica	150
Paraffin	5
Shellac	15
Medium-process oil	10
Litharge	20
Cure at 287° F (min.)	30

Temperature (° C)	Resistivity (ohm-cm.)
25	5.46×10^{12}
40	1.13×10^{12}
60	1.62×10^{11}
80	6.01×10^{10}
100	1.89×10^{10}

There are electrical conditions under which the decrease of resistivity with rising temperature even up to 100° C could be permitted, and there are more severe conditions under which high-temperature applications would invite failure. It is not easy to state in a general way what the allowable limits are, and it would be beyond the scope of this paper to attempt to do so. The limits depend on many factors, and careful analysis of high-temperature applications should be made to determine their practicability.

CONDUCTING NEOPRENE

The insulating qualities of Neoprene do not cover the entire range of electrical properties that are of technical interest today. Electrical conductivity in Neoprene is also important, and is attainable by the same means and to the same extent, as for rubber. The following data are based on established commercial products, and do not indicate the possibilities of new blacks which have recently been offered and may soon be developed. The data illustrate the range of values attainable with several types of carbon black. Litharge was not used in these formulas since its effect on insulating qualities was not required.

Base Compound

Neoprene (Type GN)	100
Hexamethyleneammonium hexamethylenedithiocarbamate	0.25
Stearic acid	0.5
Phenyl-α-naphthylamine	2
Extra-light calcined magnesia	4
Light-process oil	8
Zinc oxide	5
Carbon black	As indicated
Cure at 287° F (min.)	30

	A.C. resistivity (ohm-cm.)	
Type of black	50 parts	100 parts
Acetylene	2.7×10^{2}	1.2×10^{2}
Soft carbon	1.6×10^{8}	2.0×10^{7}
Semireinforcing	1.0×10^{8}	6.7×10^{4}
Channel	8.5×10^{7}	1.7×10^{6}

As a further illustration of the conductivity obtainable, the following data show the trend in a.c. resistivity values with increasing amounts of acetylene black:

BASE COMPOUND

Neoprene (Type GN)	100
Hexamethyleneammonium hexamethylenedithiocarbamate	0.3
Phenyl-α-naphthylamine	1
Extra-light calcined magnesia	4
Acetylene black	As indicated
Light-process oil	1
Zinc oxide	5
Cure at 287° F (min.)	30

Parts of acetylene black	A.C. resistivity (ohm-cm.)
0	1×10^{12}
10	2×10^{8}
20	9×10^{7}
30	3×10^{4}
40	6.4×10^{2}
50	1.4×10^{2}
75	1.4×10^{2}

It is not intended to go extensively into the phenomena of conducting Neoprene compositions, but the effects appear to be similar to those for rubber, which are covered extensively elsewhere[7].

The fact should be kept in mind that whether a material is a resistor or a conductor is relative. Rubber is an insulator in comparison with most metals, but it is a conductor in comparison with fused quartz and purified ceresin wax. Neoprene likewise is an insulator in comparison with most metallic elements, but whether it is an insulator or conductor with respect to rubber depends on the particular compounds compared. Figure 2 illustrates what might be called the "resistivity spectrum" for electrical materials. The horizontal axis shows the range of resistivity which has been measured, plotted logarithmically to provide a practical spread of values on the chart. At the various vertical levels the horizontal lines show the range of resistivity values which have been published in various reference works[8] in comparison with Neoprene and rubber for which values have been assumed in this paper. The range for rubber is taken to be $50–5 \times 10^{15}$ ohm-cm., although higher values have been reported for purified rubber[9]. The range for Neoprene is taken to be $50–5 \times 10^{13}$. The range for metallic elements begins with silver at 1.47×10^{-6}, and may be extended to the value for the metalloid boron at 8×10^{4}. Both Neoprene and rubber overlap this range. At the other end of the range, Neoprene overlaps published values for such insulating materials as slate, phenolic resins, fiber, Lavite, glass, porcelain, and dry wood. It does not quite attain the published value for enamel, and is distinctly inferior to the high values attained by various waxes, mica, rosin, and sulfur. This would seem to indicate rather conclusively that, since slate, fiber, Lavite, phenolic resins, glass, and porcelain are useful as insulation for low-voltage service, Neoprene may have parallel utility in combination with its other desirable properties.

An aspect of the superior resistance of Neoprene to heat is shown by Figure 3. A length of No. 14 AWG copper wire was covered with 3/62-inch Neoprene insulation, and another length was similarly insulated with heat-

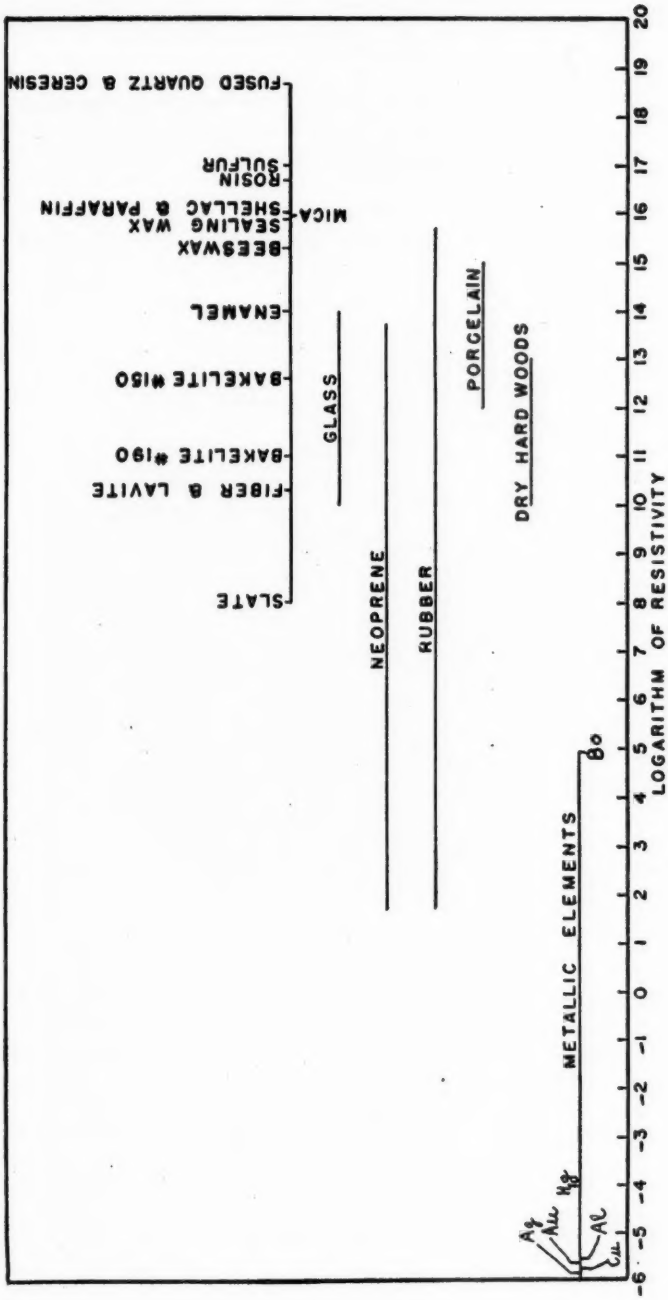

FIG. 2.—Resistivity spectrum for insulating materials.

resistant rubber. After 15 months in a 70° C air oven, both samples were wound on a half-inch mandrel. The rubber was brittle enough to crack badly, whereas the Neoprene showed no signs of failure.

Code specifications based on the characteristics of a given material are not necessarily proper criteria for other materials. For example, a code wire specification of 1500 megohms per thousand feet[10] for rubber-insulated wire is not based on the electrical demands made on this insulation, but on a characteristic value of rubber as a quality control. Specifications for Neoprene-insulated wire based on its electrical properties would be adequate to ensure satisfactory performance of the wire under many conditions of low-voltage

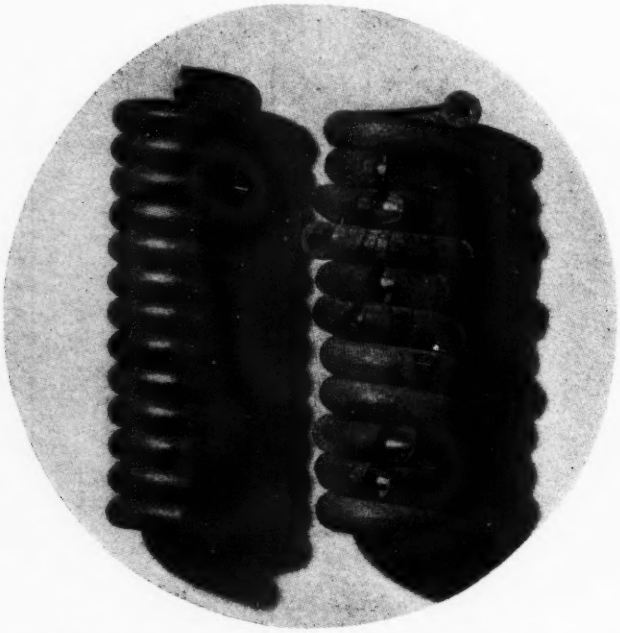

FIG. 3.—Superior resistance to heat shown by Neoprene over rubber.

service. The dielectric strength test specified for code wire, on the contrary, is not indicative of the electrical properties of rubber, but is set up as a means of detecting pinholes and other flaws in the extruding coating. The test applied to 3/64-inch wall insulation at 1500 volts works out to 32 volts per mil. This is obviously a trivial exposure for a solid film of either rubber or Neoprene, which can be made to have a dielectric strength of at least 800 volts per mil.

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